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(54) Title: SILICONE POLYMER ENCAPSULATED SUBSTRATES (57) Abstract <p>A flexible porous substrate (i.e., leather, paper, an open-celled foamed structures) comprising a matrix having open cells therein is provided wherein the cells are partially lined with a silicone polymer. Most cells remain open, but are partially filled with silicone polymer. The substrate displays characteristics not achievable in prior art substrates treated with either fluorochemical or silicone polymer, such as higher water droplet contact angle, higher abrasion resistance, and higher water rewashability, yet breathability and water repellency remain excellent. The treated substrate can display hand characteristics similar to the hand of the untreated substrate. Optionally but preferably, the substrate is preliminarily uniformly impregnated with a fluorochemical. Also optionally, the substrate can be post treated with fluorochemical to improve characteristics, such as oil penetration and soil resistance. The substrate is produced by using a pressure impregnation technique upon a substrate using a curable silicone polymer composition.</p>		

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SILICONE POLYMER ENCAPSULATED SUBSTRATES

REFERENCE TO RELATED PATENT APPLICATIONS

5 This application is a continuation-in-part of
my earlier filed U.S. Patent Application Serial Nos.
167,630; 167,643; 167,797; and 167,869 all filed March
14, 1988.

BACKGROUND OF THE INVENTION

Field of the Invention

10 The present invention generally concerns
porous substrates that are modified in their properties
by incorporation therein of silicone polymer. Such
substrates are prepared by impregnation methods that
encapsulate passageways through the substrate matrix or
15 line at least some of the open pores or cells comprising
the substrate with silicone polymer while leaving at
least some of the open pores or cells of the substrate
open.

Prior Art

20 In the prior art, it has been proposed to
treat porous webs and substrates, especially fabrics,
with silicone resins and also with fluorochemicals.

Conventional treatments of webs fall into the
general categories of (i) coatings and (ii) saturations
25 and impregnations.

For example, U.S. Patents Nos. 3,436,366;
3,639,155; 4,472,470; 4,500,584; and 4,666,765 disclose
silicone coated fabrics. Silicone coatings are known to
exhibit relative inertness to extreme temperatures of
30 both heat and cold and to be relatively resistant to
ozone and ultraviolet light. Silicone coatings can also
selectively exhibit resistance to soiling, strength
enhancement, and/or flame retardancy.

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Fluorochemical treatment of webs is known to impart properties, such as soil resistance, grease resistance, and the like.

5 Prior art fluorochemical and silicone fabric treatment evidently each can protect only that side of the fabric upon which they are disposed. Such treatments characteristically significantly alter the hand, or tactile feel, of the treated side. Prior
10 silicone fabric coatings typically degrade the tactile finish, or hand, of the fabric and give the coated fabric side a rubberized finish which is not appealing for many fabric uses, particularly garments.

U.S. Patent No. 4,454,191 describes a
15 waterproof and moisture-conducting fabric coated with a hydrophilic polymer described as a compressed foam of an acrylic resin modified with polyvinyl chloride or polyurethane. The polymer serves as a sort of "sponge" soaking up excess moisture vapor.

20 Other microporous polymeric coatings have been used in prior art attempts to make a garment breathable, yet waterproof.

Various polyorganosiloxane compositions are taught in the prior art that can be used for making coatings that impart water-repellency to fabrics.
25 Typical of such teachings is the process described in U.S. Patent No. 4,370,365 which describes a water repellent agent comprising, in addition to an organohydrogenpolysiloxane, either one or a combination of linear organopolysiloxanes containing alkene groups,
30 and a resinous organopolysiloxane containing tetrafunctional and monofunctional siloxane units. The resultant mixture is catalyzed for curing and dispersed in an aqueous emulsion. The fabric is dipped in the emulsion and heated. The resultant product is said to
35 have a good "hand" and to possess waterproofness.

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This type of treatment for rendering fabrics water repellant without affecting their "feel" is common and well known in the art. However, it has not been shown that polyorganosiloxanes have been coated on fabrics in such a way that both high levels of resistance to water by the fibers/filaments and high levels of permeability to water vapor are achieved. As used herein, the term "high levels of permeability to water vapor" has reference to a value of at least about 500 gms/m²/day, as measured by ASTM E96-80B. Also, as used herein, the term "high level of waterproofness" is defined by selective testing methodologies discussed later in this specification. These methodologies particularly deal with water resistance of fabrics and their component fibers.

Porous substrates have been further shown to be surface coated in, for example, U.S. Patent Nos. 4,478,895; 4,112,179; 4,297,265; 2,893,962; 4,504,549; 3,360,394; 4,293,611; 4,472,470; and 4,666,765. These surface coatings impart various characteristics to the surface of a substrate, but do not substantially impregnate the web fibers. Such coatings remain on the surface and do not provide a film over the individual internal fibers and/or yarn bundles of the substrate. In addition, such coatings on the web surface tend to wash away quickly.

Prior art treatments of substrates, by saturation or impregnation also suffer from limitations. Saturation, such as accomplished by padbath immersion, or the like, is capable of producing variable concentrations of a given saturant chemical.

In order to treat a flexible substrate, by heavy saturation, or impregnation, with a polymer material, such as a silicone resin, the prior art has suggested immersion of the flexible substrate, or

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5 fabric, a padbath, or the like, using a low viscosity liquid silicone resin so that the low viscosity liquid can flow readily into, and be adsorbed or absorbed therewithin. The silicone resin treated substrate is typically a rubberized web, or fabric, that is very heavily impregnated with silicone. Such a treated substrate is substantially devoid of its original tactile and visual properties, and instead has the characteristic rubbery properties of a cured silicone polymer.

10 U.S. Patent No. 2,673,823 teaches impregnating a polymer into the interstices of a fabric and thus fully filling the interstices. This patent provides no control of the saturation of the fabric. It teaches a full saturation of the interstices of the fabric.

15 The prior art application of liquid or paste compositions to textiles for purposes of saturation and/or impregnation is typically accomplished by an immersion process. Particularly for flexible substrates, including fabric, an immersion application of a liquid or paste composition to the substrate is achieved, for example, by the so-called padding process wherein a fabric material is passed first through a bath and subsequently through squeeze rollers in the process sometimes called single-dip, single-nip padding.

20 Alternatively, for example, the fabric can be passed between squeeze rollers, the bottom one of which carries the liquid or paste composition in a process sometimes called double-dip or double-nip padding.

25 Coating at a predetermined thickness can be achieved by using precision-controlled deposition of coating material followed by passage through a pair of opposed scraping knives. The knives smooth the coating and maintain the thickness of the coating to a desired thickness. For example, it is possible to apply a

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relatively thick silicone liquid elastomer coating to a rough substrate, typically fiberglass, in order to make architectural fabric as is taught in U.S. Patent No. 4,666,765. In this example, the drag knives are set to a thickness of about 2 to 10 mils thicker than the thickness of the substrate. This setting, depending on the coating speed, can yield a base coat thickness of approximately 3 to 12 mils thicker than the substrate thickness.

Various types of coatings, and various coating thicknesses, are possible. However, a general principle of coating machinery is that the coating material is swept, or dragged, along the surface of the fabric. No special attention is normally given to any pressured forcing of the coating into the fabric, therein making the coating also serve as an impregnant. Of course, some coating will be urged into surface regions of the fabric by the coating process. Generally, however, application of high transversely exerted (against a fiber or surface) forces at the location of the coating deposition and/or smoothing is not desired in the prior art processes because it is the goal of a prior art coating processes to leave a definite thickness of coating material upon a fabric, and not to scrape the fabric clean of surface-located coating material.

One useful silicone polymer composition is taught by U.S. Patent Nos. 4,472,470 and 4,500,584, and includes a vinyl terminated polysiloxane, typically one having a viscosity of up to about 2,000,000 centipoise at 25°C, and a resinous organosiloxane polymer. The composition further includes a platinum catalyst, and an organohydrogenpolysiloxane crosslinking agent, and is typically liquid. Such composition is curable at temperatures ranging from room temperature to 100°C or higher depending upon such variables as the amount of

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platinum catalyst present in the composition, and the time and the temperature allowed for curing.

Such compositions may additionally include fillers, including finely divided inorganic fillers.

5 Silicone resin compositions that are free of any fillers are generally transparent or translucent, whereas silicone resin compositions containing fillers are translucent or opaque depending upon the particular filler employed. Cured silicone resin compositions are
10 variously more resinous, or hard, dependent upon such variables as the ratio of resinous copolymer to vinyl terminated polysiloxane, the viscosity of the polysiloxane, and the like.

15 Curing (including polymerization and cross-linking) can encompass the same reactions. However, in the fabric finishing arts, such terms can be used to identify different phenomena. Thus, controllable and controlled curing, which is taught by the prior art, may not be the same as control of crosslinking. In the
20 fabric finishing arts, curing is a process by which resins or plastics are set in or on textile materials, usually by heating. Crosslinking may be considered to be a separate chemical reaction from curing in the fabric finishing arts. Crosslinking can occur between
25 substances that are already cured. Crosslinking can stabilize fibers, such as cellulosic fibers through chemical reaction with certain compounds applied thereto. Crosslinking can improve mechanical factors such as wrinkle performance. Polymerization can refer
30 to polymer formation or polymer growth.

SUMMARY OF THE INVENTION

35 This invention relates to a flexible porous substrate having generally open cells or pores therein. The substrate is preferably microcellular and has at least some of its cells or pores at least partially

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lined with a silicone polymer composition which is preferably cured. At least some of said cells remain open after being treated with the silicone polymer. The substrate can also be considered to have encapsulated passageways through its matrix.

5 The silicone polymer composition has a viscosity that is sufficient to line the cells or encapsulate the passageways. Generally the viscosity is greater than about 1,000 centipoise and less than about 10 2,000,000 centipoise. Such composition, when cured, is preferably elastomeric.

Preferably, a fluorochemical is impregnated into said substrate before cells or pores are lined with silicone polymer.

15 In substrates of this invention, the quantity of silicone polymer can vary widely but it is an amount sufficient to line the cells or pores of the substrate. Generally, the amount is in the range of about 5 to about 200 weight percent of the weight of the untreated 20 substrate. When present, the quantity of fluorochemical is in the range of about 0.01 to about 5 weight percent of the untreated substrate. When, as is preferred, a substrate incorporates both a fluorochemical and a silicone polymer, the total weight of said 25 fluorochemical and said silicone polymer is in the range of about 5 to about 200 weight percent of the weight of the untreated substrate.

Notwithstanding the large amount of silicone present in substrates of the present invention, they 30 surprisingly retain porosity, breathability, flexibility, hand and other characteristics similar to untreated webs while exhibiting improved characteristics such as water repellancy, rewashability, service life, abrasion resistance and durability.

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The porous substrates are generally flat or planar and can be regarded as a porous matrix. The substrate or matrix can contain dispersed materials, including particulates, fibers, binders, and the like. Such a substrate or matrix can be a natural or synthetic (man-made) material.

If present, fibers can be in the form of monofilaments, yarn, staples, or the like. Such fibers can be made from a synthetic polymer or a natural fibrous material. Presently preferred synthetic polymers include polyamides (nylons), acrylics, polyesters, such as polyethylene terephthalate, polyolefins such as polypropylene and polyethylene, regenerated cellulose, cellulose acetates, and the like. Presently preferred natural fibers include cotton, linen, wool, silk and wood.

A porous substrate of the present invention contains a cured silicone polymer impregnant that is present as a film, sheath, coating or layer that lines at least a portion of the open cells or pores and forms an encapsulating layer on the passageway through the substrate matrix. In a presently preferred embodiment, substantially all of the open cells or pores are substantially completely lined. Most of the cells or pores of the substrate are at least partially unfilled (i.e., unplugged) by impregnant, and, in a presently preferred embodiment, are substantially completely unfilled by impregnant. The outer surfaces of the substrate are preferably substantially free of impregnant.

At a microscopic level, a substrate of the present invention, for example, a natural or synthetic leather, can be regarded as being a complex structure, but generally the discreteness of a major portion of the

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lined cells or pores is discernable under microscopic examination.

Paper is also a complex structure which can comprise fibers defining the walls of open pores or cells of a matrix. With paper, a substantially complete polymer encapsulation of the matrix does not mean that each and every pore or cell within the matrix is uniformly and individually substantially completely lined with silicone polymer regardless of location. However, a substantial part of that portion of the paper where encapsulation is desired, e.g., at one or both surfaces or throughout, is generally encapsulated. Further, due to the fibrous nature of the matrix, some encapsulation or coating of individual fibers which form the matrix may occur as well as the lining of the pores or cells.

Silicone polymer encapsulation of the passageways in a substrate (or lining of open cell walls) which substantially completely lines a substrate's cells while leaving the substrate's cells substantially completely unplugged with polymer means that the silicone polymer is located mostly upon surface portions of the cells or pores of the substrate.

Depending upon the conditions used to produce it, a cell or pore lined substrate produced in accordance with the present invention can characteristically and preferably exhibit a soft hand and flexibility that is comparable, essentially equivalent or similar to the hand and flexibility of the untreated substrate. In some cases the difference in hand between the treated and untreated substrates may not be perceptible. This is particularly surprising in view of the substantial amounts of silicone polymer being added to the substrate. A cell lined substrate has a breathability which, by a present preference, can

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approach that of the untreated substrate notwithstanding the relatively large amounts of silicone polymer present.

5 A silicone polymer composition having a viscosity in the range above indicated is used to produce the treated substrates. If desired, additives can be admixed with such a composition to adjust and improve properties of the composition or substrate, such as viscosity and/or rheology, combustibility,
10 breathability, flexibility, reflectivity, conductivity, light fastness, mildew resistance, rot resistance, stain resistance, grease resistance, and the like. In general, a substrate of this invention exhibits enhanced durability.

15 A cell or pore lined substrate of the present invention preserves much, or even substantially all, of its original untreated hand even after an extended period of use. In contrast, an untreated substrate typically loses its original hand after an extended
20 period of use. This is achieved by the cell or pore silicone polymer wall lining that preserves fluorochemical properties. This is thought to prevent new surfaces from being exposed, thereby minimizing the amount of untreated surfaces that degrade much faster
25 than untreated surfaces.

A cell or pore lined substrate of this invention can undergo a large number of machine washings with detergent without experiencing appreciable or significant change or deterioration.

30 The silicone polymer composition substantially prolongs the use and service life of a substrate, usually by at least an order of magnitude, depending on such factors as substrate type, extent and type of treatment by the teachings of this invention, and the
35 like.

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Optionally, and as indicated above, agents or additives carried by the silicone polymer composition into a substrate can be stably fixed in the substrate with the cured silicone polymer. For example, agents such as ultraviolet light absorbers, dulling agents, reflectivity enhancers, and the like, which modify a substrate's response to light and radiation are desirably located substantially upon the surfaces of the substrate's structural elements. When these agents are incorporated into the silicone polymer film, it appears that then they are retained where they are deposited.

One presently preferred class of viscous curable liquid silicone polymer compositions useful in the invention contains a substituted benzophenone.

In addition, the present invention is directed to processes for making silicone polymer open cell or pore lined substrates. Such processes involve tensioning a porous, flexible substrate, applying a curable silicone polymer composition thereto, and then moving a generally uniformly applied localized shear force over and against one surface of the tensioned substrate. The shear force is sufficient to shear thin the silicone polymer, to distribute the silicone polymer composition within the substrate, to at least partially individually line wall surface portions of at least some of the substrate, and to leave at least some of the substrate open (and not filled or plugged with such composition). The resulting substrate is then optionally interveniently stored or is (preferably) immediately subjected to curing conditions (heat, moisture and/or radiation) which converts the polymer composition as deposited in the substrate into a solid elastomeric polymer.

Various other and further features, embodiments, and the like which are associated with the

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present invention will become apparent and better understood to those skilled in the art from the present description considered in conjunction with the accompanying drawings wherein presently preferred
5 embodiments of the invention are illustrated by way of example. It is to be expressly understood, however, that the drawings and the associated accompanying portions of this specification are provided for purposes of illustration and description only, and are not
10 intended as limitations on the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings:

Fig. 1 is a graphical plot illustrating the flow of the silicone polymer composition over time upon and in substrates both pretreated and untreated with
15 water repellent chemicals, such as fluorochemicals;

Fig. 2 is a view of the surface of an untreated leather magnified 100 times;

Fig. 3a is a view of the surface of a treated leather of the present invention magnified 100 times;
20

Fig. 3b is a cross sectional view of the silicone polymer impregnated leather of Fig. 3a;

Figs. 4a and 4b illustrate diagrammatically one embodiment of an apparatus suitable for use in the
25 practice of the present invention;

Fig. 5 is a diagrammatic representation illustrating the process in accordance with the present invention;

Fig. 6 illustrates diagrammatically another embodiment of an apparatus suitable for use in the
30 practice of the present invention;

Fig. 7 illustrates diagrammatically another embodiment of an apparatus suitable for use in the practice of the present invention;

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Figs. 8a through 8d are graphs illustrating ways of plotting rheological behavior;

Fig. 9 is a schematic vector diagram illustrating surface tension forces;

5 Fig. 10 is a graph relating contact angle over a smooth, solid surface;

Figs. 11a through 11d show representative velocity profiles; and

10 Figs. 12a through 12c illustrate diagrammatically another and presently preferred embodiment of apparatus suitable for use in the practice of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 A flexible porous substrate having open cells which is used as a starting material in this invention is generally and typically essentially planar or flat and has generally opposed, parallel surfaces. Such a substrate is a three-dimensional structure and has open cells that can, and typically do, comprise pores or void spaces in such a substrate. The substrates are typically regarded as being matrix structures or bodies which can include fibrous and non-fibrous elements. Flexible porous substrates used as starting materials in the practice of this invention are breathable and
25 moisture vapor permeable.

The term "breathable" as used herein, refers to the ability of the flexible porous substrates to allow moisture vapor to permeate or transport through its structure. The mechanism for transport is not
30 important but the ability of the porous substrate to continue to transport moisture vapor at a level that is a percentage of the original unimpregnated material is important. One method of measuring the rate of the moisture vapor transport is the American Society for
35 Testing and Materials (ASTM) Test Method E-96-80. In

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this method, a substrate sample is attached to the opening of a vessel filled with water. The substrate is attached with a substance such as wax or chalking to prevent water vapor from leaking at the fabric/vessel junction. The vessel is placed in a chamber with controlled temperature and humidity depending on the desired test conditions. Following a 24 hr period, the vessel is weighed to determine the water lost. With the known area of fabric exposed to high moisture vapor content in the vessel, a rate of moisture vapor transmission expressed in grams per square meter per day can be determined and compared to the original, unimpregnated material.

Presently preferred classes of substrates are paper, leathers (including natural leathers, and man-made or synthetic leathers), and foamed plastic sheets (or films) having open cells.

As those skilled in the art appreciate, foamed plastic sheet or film substrates are produced either by compounding a resin and a foaming agent or by injecting air or a volatile fluid into a liquid polymer while it is being processed into a sheet or film. A foamed substrate has an internal structure characterized by a network of gas spaces, or cells, that make the substrate less dense than the solid polymer. The foamed sheets or film substrates used as starting materials in the practice of this invention are flexible, open-celled structures. Examples include chloroprene, neoprene, and the like.

The class of foamed substrates known as "structural foams" is not suitable for use in the practice of this invention since such substrates have a solid skin which is believed to be substantially non-porous that is integral with and overlies a cellular core.

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Natural leathers suitable for use in this invention are typically split hides. Commercially, leathers are usually sold as weight grades (kg/in^2 or oz/ft^2) rather than by gauge (run or mils). A present
5 preference is to employ leathers having grades in the range of about 2 to about 4 oz/ft^2 but higher and lower grades can be used without departing from the spirit and scope of this invention.

Synthetic leathers as a class have wide
10 variations in composition, structure and properties. Synthetic leathers can be divided into two general categories: coated fabrics and poromerics.

Synthetic leathers which are poromerics, as those skilled in the art appreciate, are manufactured so
15 as to resemble leather closely in breathability and moisture vapor permeability, as well as in workability, machinability, and other properties. The barrier and permeability properties normally are obtained by manufacturing a controlled microporous structure.

Synthetic leathers which are coated fabrics, as those skilled in the art appreciate, like poromerics, have a balance of physical properties and economic
20 considerations. Usually the coating is either vinyl or urethane. Vinyl coatings can be either "solid" or so-called "expanded vinyl" which has internal air bubbles. Because such structures usually have a non-porous
25 exterior or front surface or face, they display poor breathability and moisture vapor transmission. However, since the interior or back surface or face is porous,
30 such a coated fabric can be used in the practice of this invention by applying the silicone polymer to the back face.

The substrates utilized in this invention can have complex structures. For example, the substrates
35 can be made from a polymeric material, in a matrix or

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shaped form. They can include fibrous material or fibers and non-fibrous material. They can be comprised of natural or synthetic material. Examples of non-fibrous material are particulate fillers, binders, dyes, sizes, and the like. Synthetic leathers, are now believed to contain at least about 35 weight percent of fibers or fibrous materials. It is presently preferred that substrates be untreated with any sizing agent, coating, or the like, except as taught herein.

While fibers having a length to width ratio of about 100:1 are preferred, shorter fibers can be used. For example, short fibers can be present in a matrix type of substrate and can serve as a reinforcing material, filler, or the like. Cellulosic fibers and proteinaceous fibers, for example, can be used herein as can synthetic fibers, as hereinbelow described.

The term "fiber" as used herein has general reference to a pliable, cohesive, natural, or man-made (synthetic) thread-like object, such as a monofilament, staple, filament, or the like. Fibers can be regarded as being in the form of units which can be formed by known techniques into yarns or the like. Fibers can be formed by known techniques into woven or non-woven fabrics, including weaving, knitting, braiding, felting, twisting, matting, needling, pressing, and the like for use in substrates. Preferably, fibers, such as those used for spinning, as into a yarn, or the like, have a length of at least about 5 millimeters. Fibers such as those derived from cellulosics of the type produced in paper manufacture can be used in combination with longer fibers, as above indicated, as those skilled in the art will readily appreciate.

The fibers used in a porous flexible substrate used in the practice of the present invention can be of natural or synthetic origin. Mixtures of natural fibers

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and synthetic fibers can also be used. Examples of natural fibers include cotton, wool, silk, jute, linen, and the like. Examples of synthetic fibers include rayon, acetate, polyesters (including
5 polyethyleneterephthalate), polyamides (including nylon), acrylics, olefins, aramids, azlons, glasses, modacrylics, novoloids, nitrils, rayons, sarans, spandex, vinal, vinyon, and the like.

10 In general, substrates used in the practice of this invention usually and preferably have thicknesses less than about 5 millimeters, and more preferably less than about 2.5 millimeters.

The term "elastomeric" as used herein refers to the ability of a cured silicone polymer treated
15 substrate to stretch and return to its original state.

The term "impregnation" or "impregnate", as used herein, refers to forcing a liquid substance into a porous, solid, flexible substrate.

20 With respect to the fluorochemical liquid dispersions or solutions used for substrate pretreatment, the term "impregnation" has reference to the penetration of such dispersions into a porous substrate, and to the distribution of such dispersion or solution in a preferably substantially uniform and
25 controlled manner in such substrate.

With respect to the silicone polymer compositions used in this invention, the term
"impregnation" has reference to the penetration of such
polymeric compositions into a porous substrate, to the
30 distribution of such composition in a controlled manner and through such substrate, and to the resultant at least partial lining of at least a portion of the open cells or pores of such substrate by such composition in accordance with the present invention.

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The term "coating" as used herein, refers to a generally continuous film or layer formed by a material over or on a surface.

5 The term "lining", or "lined", or the like, refers to a layer or coating on an inside wall portion of an open cell.

10 The term "encapsulation", or "encapsulate", as used herein, refers to the partial or complete surrounding, encasement, or enclosing by a discrete layer, film, coating, or the like, of passageways in the matrix of a substrate or the lining of the cells or pores of a substrate.

15 The term "curing", or "cure", as used herein, refers to a change in state, condition, and/or structure in a material, such as a curable silicone polymer composition that is usually, but not necessarily, induced by at least one applied variable, such as time, temperature, radiation, presence and quantity in such material of a curing catalyst or curing accelerator, or
20 the like. In the occurrence of curing in any given case, such as the curing of a polymer composition that has been impregnated into a porous flexible substrate, the components of such a composition may experience occurrence of one or more of complete or partial (a)
25 polymerization, (b) cross-linking, or (c) other reaction, depending upon the nature of the composition being cured, application, and presumably other factors.

The term "filled" as used herein in relation to open cells or pores, and to the amount of silicone
30 polymer composition therein in a given substrate, designates the presence of such composition therein. When a given open cell or pore is totally taken up by such composition, it is "completely filled" or "plugged".

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Measurements of the degree of structural element encapsulation, open cell, pore lining, fillage, plugging, or the like, are conveniently made by microscopy, or preferably by conventional scanning electron microscopy (SEM). Because of the nature of such measuring by SEM for purposes of the present invention, "a completely filled" open cell can be regarded as a "plugged" open cell, for example.

A flexible, porous substrate is preferably untreated or scoured before being treated in accordance with the present invention. Preferably the substrate is preliminarily treated, preferably saturated, for example, by padding, to impregnate the substrate with a fluorochemical. Typically, and preferably, the treating composition comprises a dispersion of fluorochemical in a liquid carrier. The liquid carrier is preferably aqueous and can be driven off with heat after application. The treating composition has a low viscosity, typically comparable to the viscosity of water or less. After such a treatment, it is presently preferred that the resulting treated substrate exhibits a contact angle with water measured on an outer surface of the treated substrate that is greater than about 90 degrees. The treated substrate preferably contains fluorochemical substantially uniformly distributed therethrough. Thus, the fluorochemical is believed to be located primarily on the surface of the cells in the substrate.

A sufficient and presently preferred concentration of fluorochemical in a treatment composition is typically in the range of about 1 to about 10% by weight based on total composition weight, and more preferably is about 2.5% of an aqueous treating dispersion. Substrate weight add-ons of the fluorochemical can vary depending upon such factors as

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the particular substrate treated, the silicone polymer impregnant to be utilized in the next step of the process of this invention, the intended use and properties of the treated substrates of this invention, and the like. The fluorochemical weight add-on is typically in the range of 0.01 to about 5% of the weight of the untreated substrate. After fluorocarbon impregnation, the treated substrate is preferably padded to remove excess fluorochemical composition after which the substrate is heated or otherwise dried to evaporate carrier liquid and thereby also accomplish fluorochemical insolubilization or sintering, if permitted or possible with the particular composition used.

The fluorochemical treated substrate is thereafter impregnated under pressure by the procedures taught by this invention, with a predetermined amount of a curable silicone polymer impregnant composition to form a substrate whose open cells are at least partially lined with the curable impregnant, whose substrate outer surfaces are substantially free of the curable impregnant, and whose cells are not completely filled with the curable impregnant. The curable impregnant composition utilized preferably exhibits a viscosity greater than 1,000 centipoise and less than 2,000,000 centipoise at rest at 25°C at a shear rate of 10 reciprocal seconds.

The curable silicone impregnant composition is believed to be typically polymeric, to be usually a mixture of co-curable polymers and oligomers, and to include a catalyst to promote the cure.

The silicone polymer impregnant composition can include, as additive components, polyurethanes, fluorosilicones, silicone-modified polyurethanes,

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acrylics, polytetrafluoroethylene-containing materials, and the like.

5 The substrate is thereafter cured to convert the curable silicone polymer composition into a solid elastomeric polymer.

It is to be understood that the depth of silicone polymer impregnation into a porous substrate can be controlled by the application procedures herein described to provide a selective placement of the
10 silicone polymer impregnant within the substrate. This placement allows the shear thinning, i.e. viscosity reduction, action to take place selectively throughout the substrate.

The fluorochemical residue that remains after
15 fiber treatment may not be exactly evenly distributed throughout the substrate, but may be present in the substrate in certain discontinuities. For example, these discontinuities may be randomly distributed small areas upon an individual cell or pore wall. However,
20 the quantity and distribution of fluorochemical through a substrate is believed to be largely controllable. Some portions of the fluorochemical may become dislodged from the substrate and migrate through the silicone polymer to cause the shear thinning of the silicone
25 polymer.

The silicone polymer composition is theorized to be caused to flow and distribute itself through the substrate matrix and upon the walls of open cells in the substrate under the influence of the processing
30 conditions provided by this invention. This flow and distribution is further theorized to be facilitated and promoted by the presence of a fluorochemical which has been preliminarily impregnated into a substrate, as taught herein. The amount of fluorochemical or
35 fluorochemical residue in a substrate is believed to

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influence the amount, and the locations, where the liquid silicone polymer impregnant will produce an encapsulation of the passageways of the substrate matrix and lining of the open cells or pores, thereby
5 producing, if desired, a substantial encapsulation of the passageways and a lining of the open cells or pores. However, there is no intent to be bound herein by theory.

It is to be understood that the depth of
10 silicone polymer impregnation into a substrate can be controlled by the application procedures herein described to provide selective placement of the silicone polymer impregnant within the substrate.

Some portion of the residue of fluorochemical
15 resulting from a preliminary substrate saturating operation is theorized to be present upon the surface of a treated substrate after encapsulation by the silicone polymer has been achieved. This is believed to be demonstrated by the fact that a substrate exhibits an
20 enhanced water and oil repellency, typical of fluorochemicals in porous substrates. It is therefore believed that the fluorochemicals are (i) affecting the adherence of the liquid silicone polymer as a thin film encapsulating layer about the treated substrate
25 passageways and as a thin film lining on walls of open cells or pores as well as (ii) facilitating liquid silicone polymer impregnant pressurized flow within and about the open cells of the substrate being treated so that the silicone can assume its position encapsulating
30 the passageways of the substrate matrix and lining of open cells or pores.

The exact interrelationship between the silicone polymer encapsulating film and the impregnated fluorochemical is presently difficult, or perhaps
35 impossible, to quantify because of the variables

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involved and because transparent silicone polymer is difficult to observe by optical microscopy. It can be theorized that perhaps the encapsulating silicone polymer and the fluorochemical each tend to produce discontinuous films upon the passageways through a substrate matrix or cell wall surface, and that such films are discontinuous in a complimentary manner. It may alternatively be theorized that perhaps the encapsulating silicone polymer film is contiguous, or substantially so, relative to fluorochemical molecules on a structural element surface, and that the layer of silicone polymer on a structural element surface is so thin that any dislodgment of the fluorochemical may release the fluorochemical into the silicone polymer film thereby allowing the fluorine to orient with the required cure temperature of the silicone reactivating the water surface contact angle so that the water repellant properties of an underlying fluorochemical are exerable through the silicone polymer film. However, regardless of physical or chemical explanation, the combination of silicone polymer film and fluorochemical results in the passageways through a substrate's matrix being encapsulated or a cell wall lining in a substrate when this invention is practiced. After curing, the silicone polymer is permanently fixed as an encapsulating or lining material.

By using the impregnation method provided by this invention, one can achieve an impregnation of a silicone polymer composition into a porous substrate to obtain a desired treated substrate.

A curable silicone polymer such as used in the practice of this invention is applied under pressure using shear forces onto and into a substrate. The shear forces cause the curable silicone polymer to flow into the substrate. The extent of the passageways through a

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substrate's matrix encapsulation and cell wall lining is believed to be regulatable by controlling such factors as the selection and applied amount of fluorochemical and curable silicone polymer in combination with the applied compressive and shear forces employed at a given temperature so that encapsulation and cell wall lining is achieved while the open cells of the substrate are not completely filled with polymer, and the outer opposed surfaces of the substrate are substantially completely free of silicone polymer coating or residue. After such an impregnation procedure, the curable silicone polymer impregnant is then cured.

The curable silicone polymer impregnant is applied in an amount at least sufficient to partially saturate the substrate and fill or plug some of the open cells of the substrate. Then, the substrate, while tensioned, is passed over and against shearing means or through a compression zone, such as between rollers or against a shear knife. Thus transversely applied shear force and compressive pressure is applied to the web. The combination of tensioning, shearing forces, and substrate traveling speed is sufficient to cause the curable silicone polymer impregnant to flow into and around the open cells or pores of the substrate, thereby leaving the cells or pores substantially unfilled, with silicone polymer impregnant. Excess silicone polymer is removed by surface wiping action of the shearing means. The curable silicone polymer impregnant encapsulating the passageways through the substrate matrix or lining the cell or pore walls, is thereafter cured.

The desired impregnation or penetration of, and distribution of silicone polymer impregnant in, a substrate is believed to be achieved by localized pressuring forces exerted on a substrate surface which are sufficiently high to cause the viscosity of a

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silicone polymer impregnant composition to be locally reduced, thereby permitting such silicone impregnant to flow and impregnate the substrate and to encapsulate the passageways through the substrate matrix or line its cell or pore walls. To aid in this process, the substrate is preferably at least slightly distorted by tensioning or stretching, while being somewhat transversely compressed at the location of the impregnation by applied shearing force. This distortion is believed to facilitate the entrance of the silicone polymer composition into the substrate. When the compression and tension are released, the silicone polymer composition is believed to be squeezed or compressed within and through the open cells or pores of the treated substrate.

If, for example, too much silicone polymer is present in the finished product, then either or both the tension and shear force can be increased, and vice versa for too little silicone polymer. If viscous flow is not adequate through the cellular structure, producing incomplete encapsulation or lining of the cell or pore walls, then the viscosity of the silicone polymer impregnant composition can be reduced by increasing the pressures and temperatures employed for the impregnation. Alternatively, if the viscosity is excessive, then the impregnating pressure and/or temperature can be increased. Opposite adjustments should be made if silicone polymer impregnant flow is insufficiently viscous, perhaps even tending to cause a permeation of the entire matrix of the substrate. If the silicone polymer impregnating composition is resistant to being positioned in a desired location in a desired amount in a given substrate at various viscosities and/or pressures, then the level of fluorochemical pretreatment of the substrate can be

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increased, as in the case of overimpregnation, or decreased, as in the case of underimpregnation.

In one embodiment of an impregnation procedure, the pressured impregnation of a substrate occurs between two rollers. One such roller bears a silicone polymer impregnant, typically and preferably distributed uniformly upon and over a circumferentially extending textured, or gravure surface. Such roller rotates (i) in the same direction as a facing roller and (ii) oppositely to the direction of movement of a continuously moving substrate traveling past the localized impregnation area achieved between the roller and the substrate. The unidirectional rotation of the two rollers is believed to produce a distorting and stretching force or effect upon the substrate. This force is believed to promote penetration of the silicone polymer impregnant into the substrate. This form of impregnant application or coating can be termed "reverse roll coating" for convenience. Preferably the reverse coating rollers have generally horizontal axes while the moving substrate moves generally horizontally. The substrate is further concurrently both tensioned and distorted by being stretched against metering bars, bar knives, and the like which are urged against the substrate at a location which is after the location along the substrate pathway where such continuously moving substrate passes such two rollers.

Such an initial pressured impregnation stage is preferably followed by a series of further pressured substrate treatment steps believed to accomplish impregnant reintroduction, impregnant distribution, impregnant scraping, and excess impregnant removal and recovery. The collective result of such steps gradually produces a substrate wherein the silicone polymer impregnant encapsulates to a desired extent the

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passageways through the matrix of the substrate while not substantially appearing within, or collecting within, or filling beyond a desired extent, the open cells or pores of the substrate.

5 In another embodiment of an impregnation procedure, application of silicone polymer impregnant to a substrate occurs from a reservoir. This reservoir of silicone impregnant is positioned tightly against the tensioned, moving substrate. The linearly extending, 10 preferably vertically upwardly moving, substrate, constitutes a wall portion of the reservoir. Next, along the path of substrate travel, a bar or shear knife is pressed strongly and transversely against and laterally across the tensioned substrate. Further along 15 the path of substrate movement, a shear blade or flexible scraper knife is also strongly and transversely forced laterally across and against the tensioned substrate. More than one shear knife, or more than one flexible compressive knife, can be successively 20 positioned along the path of substrate movement. These blade means are believed to reintroduce the silicone polymer impregnant into the substrate, to distribute the silicone polymer, and to promote and complete the encapsulation of passageways through the substrate 25 matrix or line the cell walls with silicone polymer. These scraper knives or shear blades are also believed to force the silicone polymer impregnant further into the three-dimensional structure of the substrate. Also, these knives, particularly the scraper knives, wipe or 30 scrape excess silicone polymer impregnant off the surface of the substrate, thereby regulating the amount of silicone polymer impregnated.

 The transversely applied shear forces applied across and against the substrate are sufficiently high 35 to achieve temporarily and locally a lowering of the

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viscosity of the preferably thixotropic viscous silicone polymer impregnant. The silicone polymer impregnant is thus enabled to flow into, and upon, the internal three-dimensional structure of the substrate. Because the
5 silicone polymer composition that is being applied is subject to cure with heat or radiation and time, and because the pressured impregnation is believed to produce localized heat, the shearing conditions used prior to curing are preferably controlled to minimize
10 premature curing. The properties of the silicone polymer impregnant are preferably selected to be such that cure, or excessive cure, thereof does not occur while the substrate is being treated with silicone polymer during the pressured impregnation. The cure
15 occurs preferably only after the impregnation procedure has been completed. Preferably, the cure temperature of the silicone polymer composition is relatively high (preferably above about 250°F) and the heat exposure time is such as is needed to obtain a desired solid
20 resilient elastomeric silicone polymer in one embodiment of an impregnation procedure (Figs. 6 and 12).

If desired, the rheology of the silicone polymer impregnant may be altered or controlled. Characteristics of a treated substrate are believed to
25 be influenced by rheology, but it is believed that, in general, this invention can be practiced without careful control of rheology while controlling viscosity.

The viscosity of the silicone polymer impregnant is preferably lowered by the high pressure
30 (shear) forces exerted during pressured impregnation. However, such a pressure- and/or temperature-induced lowered viscosity should not go down too low, otherwise the impregnant can flow substantially uncontrolled in the substrate in the manner of a low viscosity liquid
35 that is saturated and impregnated into a substrate as in

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the prior art substrate treatments. If the viscosity of the silicone polymer composition is too low at the time of impregnation, then the substrate open cells can become excessively filled therewith, and the impregnant is not, for example, reliably and controllably applied to achieve an encapsulation of the passageways of the substrate matrix or lining of the cell walls of the substrate being treated.

Substituted benzophenones, and particularly 2,4-dihydroxybenzophenone, are believed to be a particularly useful class of additives to the starting silicone polymer composition, as hereinbelow described.

As above indicated, the activity transpiring at a final step in the practice of a method of this invention is generically referred to herein as curing. Conventional curing conditions known to the prior art for curing silicone polymer compositions are generally suitable for use in the practice of this invention. Thus, temperatures in the range of about 160°F to about 260°F can be used, and times in the range of about 30 seconds to about 3 minutes can be used, although longer and shorter curing times and temperatures may be used, if desired, when thermal curing is practiced. Radiation curing, as with an electron beam or ultraviolet light can also be used. However, using platinum catalysts to accelerate the cure while using lower temperatures and shorter cure times is preferable.

Because the encapsulated passageways of the substrate matrix and lined cells or pores remain open in cured substrates of this invention, the substrates are characteristically air permeable.

As indicated above, a substrate is preferably pretreated and impregnated with a fluorochemical prior to being impregnated under pressure with a silicone polymer composition as taught herein.

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The fluorochemical impregnation is accomplished preferably by first saturating a substrate with a liquid composition which incorporates the fluorochemical, and then, thereafter, removing the
5 excess liquid composition and residual carrier fluid by draining, compression, drying, or some combination thereof from the treated substrate.

It is now believed that any fluorochemical known in the art for use in substrate treatment in order
10 to achieve water repellency, soil repellency, grease repellency, or the like, can be used for purposes of practicing the present invention.

It is believed that a typical fluorochemical of the type used for substrate treatment can be
15 characterized as a compound having one or more highly fluorinated portions, each portion being a fluoroaliphatic radical or the like, that is (or are) functionally associated with at least one generally non-fluorinated organic portion. Such organic portion can
20 be part of a polymer, part of a reactive monomer, a moiety with a reactable site adapted to react with a binder, or the like.

Such a compound is typically applied to a substrate as a suspension or solution in either aqueous
25 or non-aqueous media. Such an application may be conventionally carried out in combination with a non-fluorine or fluorine containing resin or binder material for the purpose of providing improved durability as regards such factors as laundering, dry cleaning, and
30 the like.

Fluorochemicals are sometimes known in the art as durable water repellant (DWR) chemicals, although
such materials are typically believed to be not particularly durable and to have a tendency to wash out
35 from a substrate treated therewith. In contrast,

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encapsulated substrates of this invention which have been pretreated with a fluorochemical display excellent durability and washability characteristics. Indeed, the combination of fluorochemical pretreatment and silicone polymer encapsulation as provided by the present invention appears to provide a synergistic property enhancement because the effects or properties obtained appear to be better than can be obtained than by using either the fluorochemical or the silicone polymer alone for substrate treatment as practiced in the prior art.

Exemplary useful water repellent fluorochemical compositions include the compositions sold under the name Milease^R by ICI Americas Inc. with the type designations F-14N, F-34, F-31X, F-53. Those compositions with the "F" prefix indicate that they contain a fluorochemical as the principal active ingredient. More particularly, Milease^R F-14 fluorochemical, for example, is said to contain approximately 18 percent perfluoroacrylate copolymer, 10 percent ethylene glycol (CAS 107-21-1) and 7 percent acetone (CAS 67-64-1) dispersed and dissolved in 65 percent water. Milease[®] F-31X is said to be a dispersion of a combination of fluorinated resin, acetone, and water.

Still another suitable class of water repellent chemicals is the Phobotex[®] chemicals of Ciba/Geigy identified as Phototex[®] FC104, FC461, FC731, FC208 and FC232 which are each believed to be suitable for use, typically in approximately a 5 percent concentration, in saturating a substrate for use in the invention. These and many other water repellent fluorochemicals are believed to be capable of creating a surface contact angle with water of greater than about 90 degrees when saturated into a substrate and to be suitable for use in the practice of this invention.

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Another group of useful water repellent fluorochemicals is the TEFLON®-based soil and stain repellents of E.I. duPont de Nemours & Co. Inc., 1007 Market Street, Wilmington, DE 19898. Suitable TEFLON® types for use in the practice of this invention include TEFLON® G, NPA, SKF, UP, UPH, PPR, N, and MLV. The active water repellent chemical of each composition is believed to be a fluorochemical in polymeric form that is suitable for dispersion in water, particularly in combination with a cationic surfactant as a dispersant. These dispersions are dilutable in all proportions with water at room temperature. One preferred class of fluorochemical treating compositions useful in the practice of this invention comprises about 1 to about 10 weight percent, more preferably about 5 weight percent of one of the above indicated TEFLON®-type water repellent fluorochemicals in water.

Another major group of suitable water repellent fluorochemical compositions useful in the practice of the invention is commercially available under the designation ZEPEL® rain and stain repellent chemicals of E.I. duPont de Nemours & Co. Inc., such as ZEPEL® water repellent chemicals types B, D, K, RN, RC, OR, HT, 6700 and 7040. Each is believed to be a fluorochemical in polymeric form that is dispersible in all proportions at room temperature. The dispersants of ZEPEL® B, D, K, and RN are believed to be cationic, while the dispersant of ZEPEL® RC is believed to be non-ionic.

As an exemplary composition, ZEPEL® 6700 is said to be comprised of 15 to 20 percent perfluoroalkyl acrylic copolymer, 1 to 2 percent alkoxylated carboxylic acid, and 3 to 5 percent ethylene glycol. Exemplary characteristics of the composition include a boiling point of 100°C at 760mm Hg and a specific gravity of

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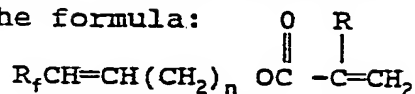
1.08. The volatiles are approximately 80 percent by weight. The pH is 2 to 5. The odor is mild; the concentrate form is that of a semi-opaque liquid; and the concentrate color is straw white. The composition and characteristics of ZEPEL® 7040 repellent chemical are believed to be substantially identical to those of ZEPEL® 6700 except that the former composition additionally contains 7 to 8 percent acetone.

Another major group of water repellent fluorochemicals comprises the Scotchgard® water repellent chemicals of 3M Co., St. Paul, Minnesota. The Scotchgard® fluorochemicals are believed to be aqueously dispersed fluorochemicals in polymeric form. The compositions of two suitable such Scotchgard® water repellent fluorochemicals are believed to be disclosed in U.S. Patent Nos. 3,393,186 and 3,356,628, which patents are incorporated herein by reference. Thus, the Scotchgard® fluorochemical of U.S. Patent No. 3,356,628 consists of copolymers of perfluoroacrylates and hydroxyalkyl acrylates. These copolymers are suitable for use as an oil and water repellent coating on a fibrous or porous surface. They have a carbon to carbon main chain and contain recurring monovalent perfluorocarbon groups having from 4 to 18 carbon atoms each and also having recurring hydroxyl radicals. From 20 to 70 percent of the weight of such copolymer is contributed by fluorine atoms in the perfluorocarbon groups and from 0.05 to 2 percent of the weight of the copolymer is contributed by the hydroxyl radicals. Such copolymer is said to have improved surface adherability properties as compared to the homopolymer of a corresponding fluorocarbon monomer.

The Scotchgard® fluorochemical of U.S. Patent No. 3,393,186 consists of perfluoroalkenylacrylates and

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polymers thereof. An exemplary preferred fluorinated monomer has the formula:



5 wherein R_f is a fluorocarbon group having from 3 to 18 carbon atoms, R is hydrogen or methyl, and n is 0-16. Such a water repellent fluorochemical composition is supplied and saturated into the substrate web as a readily pourable aqueous dispersion.

10 U.S. Patent No. 4,426,476 discloses a fluorochemical textile treating composition containing a water-insoluble fluoroaliphatic radical, an aliphatic chlorine-containing ester and a water insoluble, fluoroaliphatic radical containing polymer.

15 U.S. Patent No. 3,896,251 discloses a fluorochemical textile treating composition containing a fluoroaliphatic radical containing linear vinyl polymer having 10 to 60 weight percent fluorine and a solvent soluble carbodiimide preferably comprising
20 fluoroaliphatic groups. A table in this patent lists a plurality of prior art fluoroaliphatic radical containing polymers useful for the treatment of fabrics and the prior art patents wherein such polymers are taught.

25 U.S. Patent No. 3,328,661 discloses textile treating solutions of a copolymer of an ethylenically unsaturated fluorocarbon monomer and a ethylenically unsaturated epoxy group containing monomer.

30 U.S. Patent No. 3,398,182 discloses fluorocarbon compounds useful for fabric treatment that contain a highly fluorinated oleophobic and hydrophobic terminal portion and a different non-fluorinated oleophilic portion linked together by a urethane radical.

35 The water repellent fluorochemical compositions are preferably utilized to saturate an untreated porous

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substrate so that such composition and its constituents wet substantially completely and substantially uniformly all portions of the web. Such a saturation can be accomplished by various well known techniques, such as dipping the web into a bath of the composition, or padding the composition onto and into the web, or the like. Padding is the presently preferred method of fluorochemical application.

After application of the fluorochemical composition to the substrate, the water (or liquid carrier) and other volatile components of the composition are removed by conventional techniques to provide a treated substrate that contains the impregnated fluorochemical throughout the substrate.

In a preferred procedure of fluorochemical impregnation, a substrate is substantially completely saturated with an aqueous dispersion of a fluorochemical.

Thereafter, the resulting impregnated substrate is compressed to remove excess portions of said dispersion.

Finally, the substrate is heated to evaporate the carrier liquid. If the fluorochemical is curable, then the heating also accomplishes curing.

The fluorochemical concentration in the treating composition is such as to permit a treated fluorochemical containing substrate, after volatiles of the treating composition are removed, to exhibit a contact angle with water applied to an outer web surface which is greater than about 90° . More preferably, the contact angle provided is greater than about 130° .

The substrate weight add-on provided by the fluorochemical after removal of volatiles is usually relatively minor. However, the weight add on can vary with such factors as the nature of substrate treated,

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the type of silicone polymer impregnant utilized in the next step of the process, the temperature at which the impregnant is applied, the ultimate use contemplated for a substrate, and the like.

5 Typical weight add-ons of fluorchemical are in the range of about 0.01 to about 5 weight percent of the weight of the untreated web.

 Durability of a substrate that has been treated with a fluorochemical and durability of a
10 substrate that is subsequently treated with a silicone polymer can sometimes be improved by the conventional process of "sintering". The exact physical and chemical processes that occur during sintering are unknown. The
15 so-called sintering temperature utilized is a function of the fluorochemical composition utilized and such temperature is frequently recommended by fluorochemical manufacturers. Typically, sintering is carried out at a
20 temperature of about 130 to about 160°C for a period of time of about 2 to about 5 minutes. Acid catalysts can be added to give improved durability to laundering and dry cleaning solvents.

 The fluorochemical is believed to provide more than water or other repellency property to the treated substrate, particularly since the curable silicone
25 impregnant is often itself a water repellent.

 The precise physics and chemistry of the interaction between the fluorochemical and the silicone impregnant is not understood. A simple experiment demonstrates movement of the liquid silicone polymer as
30 influenced by the presence of the fluorochemical:

 A piece of fabric, for example the Red Kap Milliken poplin polyester cotton blend fabric, is cut into swatches. One swatch is treated with an adjuvant, for example a three percent solution of the durable
35 water-repellent chemical Milease® F-31X. The treated

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swatch and an untreated swatch are each positioned at a 45° angle to plumb. A measured amount, for example one-half ounce, of a viscous polymer composition, for example the Mobay® 2530A/B silicon composition, is dropped onto the inclined surface of each swatch. The distance in centimeters that the composition flows downwards upon the surface of the swatch is measured over time, typically for 30 minutes.

A graphical plot of the flow of the silicone composition respectively upon the untreated and treated swatch over time can be prepared, such as shown in Fig. 1. At the expiration of 30 minutes the viscous composition has typically traveled a distance of about 8.8 centimeters upon the treated swatch, or a rate of about 0.29 centimeters per minute. At the expiration of the same 30 minutes, the viscous composition has typically traveled a lesser distance of about 7.1 centimeters upon the untreated swatch, or a rate of about 0.24 centimeters per minute. Qualitatively commensurate results are obtainable with other DWR fluorochemical adjuvants that facilitate the viscous flow of polymer compositions in accordance with the related invention. Indeed, if desired, the simple flow rate test can be used to qualify an adjuvant compound for its employment within the method of the invention.

A fluorochemical treated substrate is thereafter impregnated under pressure with a predetermined amount of a curable silicone polymer impregnant composition to form a substrate where the passageways in the substrate matrix are substantially completely encapsulated with curable impregnant and whose outer surfaces and cells or pores are preferably substantially completely free of the curable impregnant. The silicone polymer impregnant is thereafter cured by heat, radiation, or the like. Even room temperature

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curing can be used. A silicone polymer impregnated, fluorochemical pretreated substrate can be interveniently stored before being subjected to curing conditions depending upon the so-called pot life of the treating silicone polymer impregnant.

A curable silicone polymer impregnant composition utilized in the practice of this invention exhibits a viscosity that is sufficient to encapsulate the passageways of a substrate matrix or line the walls of the cells or pores of a substrate. The polymer composition preferably exhibits a viscosity of greater than about 1000 centipoise and less than about 2,000,000 centipoise at 25°C at a shear rate of 10 reciprocal seconds. It is most preferred that such composition have a viscosity in the range of about 5,000 to about 750,000 centipoise at 25°C. Such a composition is believed to contain less than about 1% by weight of volatile material.

The silicone polymer is believed to be typically polymeric and to be commonly a mixture of co-curable polymers, oligomers, and/or monomers. A catalyst is usually also present, and, for the presently preferred silicone polymer compositions discussed hereinafter, is platinum or a platinum compound, such as a platinum salt.

One class of liquid curable silicone polymer compositions comprises a curable mixture of the following components:

(A) at least one organo-hydrosilane polymer (including copolymers);

(B) at least one vinyl substituted polysiloxane (including copolymers);

(C) a platinum or platinum containing catalyst; and

(D) (optionally) fillers and additives.

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Typical silicone hydrides (component A) are polymethylhydrosiloxanes which are dimethyl siloxane copolymers. Typical vinyl terminated siloxanes are vinyl dimethyl terminated or vinyl substituted polydimethylsiloxanes. Typical catalyst systems include solutions or complexes of chloroplatinic acid in alcohols, ethers, divinylsiloxanes, and cyclic vinyl siloxanes.

The polymethylhydrosiloxanes (component A) are used in the form of their dimethyl copolymers because their reactivity is more controllable than that of the homopolymers and because they result in tougher polymers with a lower cross-link density. Although the reaction with vinyl functional silicones (component B) does reportedly take place in 1:1 stoichiometry, the minimum ratio of hydride (component A) to vinyl (component B) in commercial products is reportedly about 2:1 and may be as high as 6:1. While the hydrosilation reaction of polymethylhydrosilane is used in both so called RTV (room temperature vulcanizable) and LTV (low temperature vulcanizable) systems, and while both such systems are believed to be useful in the practice of the present invention, systems which undergo curing at elevated temperature are presently preferred.

Elastomers produced from such a curing reaction are known to demonstrate toughness, tensile strength, and dimensional stability.

Particulate fillers are known to be useful additives for incorporation into liquid silicone polymer compositions. Such fillers apparently not only can extend and reinforce the cured compositions produced therefrom, but also can favorably influence thixotropic behavior in such compositions. Thixotropic behavior is presently preferred in compositions used in the practice of this invention. A terminal silanol (Si-OH) group

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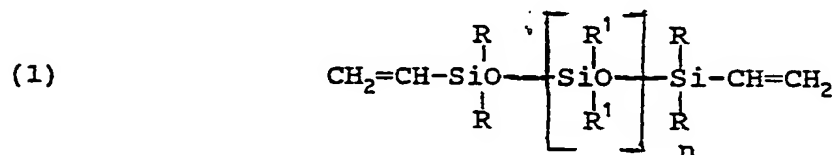
makes such silanol siloxanes susceptible to reaction in curing, as is believed desirable.

It is believed that all or a part of component B can be replaced with a so called silanol terminated polysiloxane while using an organotin compound as a suitable curing catalyst as is disclosed in U.S. Patent No. 4,162,356. However, it is presently preferred to use vinyl substituted polysiloxanes in component B.

A silicone composition useful in this invention can contain curable silicone resin, curable polyurethane, curable fluorosilicone, curable modified polyurethane silicones, curable modified silicone polyurethanes, curable acrylics, polytetrafluoroethylene, and the like.

One particular type of silicone impregnant composition which is believed to be well suited for use in the impregnation step of the method of the invention is taught in U.S. Patent Nos. 4,472,470 and 4,500,584 and in U.S. Patent No. 4,666,765. The contents of these patents are incorporated herein by reference. Such a composition comprises in combination:

(i) a liquid vinyl chain terminated polysiloxane having the formula,



wherein R and R¹ are monovalent hydrocarbon radicals free of aliphatic unsaturation with at least 50 mole percent of the R¹ groups being methyl, and where n has a value sufficient to provide a viscosity of about 500 centipoise to about 2,000,000 centipoise at 25°C;

(ii) a resinous organopolysiloxane copolymer comprising:

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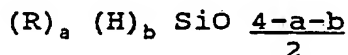
(i) $(R^2)_3SiO_{0.5}$ units and SiO_2 units,
or

(ii) $(R^3)_2SiO_{0.5}$ units, $(R^3)_2SiO$ units
and SiO_2 units, or

(iii) mixtures thereof, where R^2 and
 R^3 are selected from the group consisting
of vinyl radicals and monovalent
hydrocarbon radicals free of aliphatic
unsaturation, where from about 1.5 to
about 10 mole percent of the silicon
atoms contain silicon-bonded vinyl
groups, where the ratio of monofunctional
units to tetrafunctional units is from
about 0.5:1 to about 1:1, and the ratios
of difunctional units to tetrafunctional
units ranges up to about 0.1:1;

(iii) a platinum or platinum containing
catalyst; and

(iv) a liquid organohydrogen-polysiloxane
having the formula:



in an amount sufficient to provide from about 0.5 to
about 1.0 silicon-bonded hydrogen atoms per silicon-
bonded vinyl group of above component (i) or above
subcomponent (iii) of, R_a is a monovalent hydrocarbon
radical free of aliphatic unsaturation, a has a value of
from about 1.0 to about 2.1, b has a value of from about
0.1 to about 1.0, and the sum of a and b is from about
2.0 to about 2.7, there being at least two silicone-
bonded hydrogen atoms per molecule.

Optionally, such a composition can contain a
finely divided inorganic filler (identified herein for
convenience as component (v)).

For example, such a composition can comprise
on a parts by weight basis:

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- (a) 100 parts of above component (i);
(b) 100-200 parts of above component (ii);
(c) a catalytically effective amount of above component (iii), which, for present illustration purposes, can range from about 0.01 to about 3 parts of component (iii), although larger and smaller amounts can be employed without departing from operability (composition curability) as those skilled in the art will appreciate;
(d) 50-100 parts of above component (iv), although larger and smaller amounts can be employed without departing from operability (curability) as those skilled in the art will appreciate; and
(e) 0-50 parts of above component (v).

Embodiments of such composition are believed to be available commercially from various manufacturers under various trademarks and trade names.

As commercially available, such a composition is commonly in the two-package form (which are combined before use). Typically, the component (iv) above is maintained apart from the components (i) and (ii) to prevent possible gelation in storage before use, as those skilled in the art appreciate. For example, one package can comprise components (i) and (ii) which can be formulated together with at least some of the component (ii) being dissolved in the component (i), along with the component (iii) and some or all of the component (v) (if employed), while the second package can comprise the component (iv) and optionally a portion of the component (v) (if employed). By adjusting the amount of component (i) and filler component (v) (if used) in the second package, the quantity of catalyst

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component (iii) required to produce a desired curable composition is achieved. Preferably, the component (iii) and the component (iv) are not included together in the same package. As is taught, for example, in U.S. Patent No. 3,436,366 (which is incorporated herein by reference), the distribution of the components between the two packages is preferably such that from about 0.1 to 1 part by weight of the second package is employed per part of the first package. For use, the two packages are merely mixed together in suitable fashion at the point of use.

Other suitable silicone polymer compositions are disclosed in the following U.S. patents:

U.S. Patent No. 4,032,502 provide compositions containing a linear polydiorganosiloxane having two siloxane bonded vinyl groups per molecule, organosiloxane that is soluble in such linear polydiorganosiloxane and comprised of a mixture of a polyorganosiloxane and a polydiorganosiloxane, platinum-containing catalyst, a platinum catalyst inhibitor, and a reinforcing silica filler whose surface has been treated with an organosilicone compound.

U.S. Patent No. 4,108,825 discloses a composition comprising a triorganosiloxy end-blocked polydiorganosiloxane, an organohydrogensiloxane having an average of at least 2.1 silicon-bonded hydrogen atoms per molecule, a reinforcing silica filler having a surface treated with an organosilicone compound, a platinum catalyst, and ceric hydrate. Such silicone polymer composition is desirable when a web is being prepared which has flame retardant properties.

U.S. Patent No. 4,162,243 discloses a silicone composition of 100 parts by weight triorganosiloxy endblocked polydimethylsiloxane, reinforcing amorphous

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silica that is surface treated with organosiloxane groups, organohydrogensiloxane, and platinum catalyst.

U.S. Patent No. 4,250,075 discloses a liquid silicone polymer composition that comprises

5 vinyl-diorganosiloxy endblocked polydiorganosiloxane, polyorganohydrogensiloxane, platinum catalyst, platinum catalyst inhibitor, and carbonaceous particles. Such a silicone polymer composition is useful when a web of this invention is being prepared that has electrically
10 conductive properties.

U.S. Patent No. 4,427,801 discloses a curable organopolysiloxane of liquid triorganosiloxy endblocked polydiorganosiloxane wherein the triorganosiloxy groups are vinyl dimethylsiloxy or vinylmethylphenylsiloxy,
15 finely divided amorphous silica particles treated with mixed trimethylsiloxy groups and vinyl-containing siloxy groups, organopolysiloxane resin containing vinyl groups, organohydrogensiloxane, and a platinum containing catalyst.

U.S. Patent No. 4,500,659 discloses a silicone composition of liquid triorganosiloxy endblocked polydimethylsiloxane wherein the triorganosiloxy units are dimethylvinylsiloxy or methylphenylvinylsiloxy, a reinforcing filler whose surface has been treated with a
25 liquid hydroxyl end-blocked polyorganosiloxane which is fluorine-substituted, a liquid methylhydrogensiloxane, and a platinum-containing catalyst.

U.S. Patent No. 4,585,830 discloses an organosiloxane composition of a triorganosiloxy-
30 endblocked polydiorganosiloxane containing at least two vinyl radicals per molecule, an organohydrogensiloxane containing at least two silicone-bonded hydrogen atoms per molecule, a platinum-containing hydrosilation catalyst, optionally a catalyst inhibitor, a finely
35 divided silica filler, and a silica treating agent which

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is at least partially immiscible with said polydiorganosiloxane.

U.S. Patent No. 4,753,978 discloses an organosiloxane composition of a first diorganovinyl-siloxy terminated polydiorganosiloxane exhibiting a specified viscosity and having no ethylenically unsaturated hydrocarbon radicals bonded to non-terminal silicone atoms, a second diorganovinylsiloxy terminated polydiorganosiloxane that is miscible with the first polydiorganosiloxane and contains a vinyl radical, an organohydrogensiloxane, a platinum hydrosilation catalyst, and a treated reinforcing silica filler.

U.S. Patent No. 4,785,047 discloses silicone elastomers having a mixture of a liquid polydiorganosiloxane containing at least two vinyl or other ethylenically unsaturated radicals per molecule and a finely divided silica filler treated with a hexaorganodisilazane which mixture is then compounded with additional hexaorganodisiloxane.

U.S. Patent No. 4,329,274 discloses viscous liquid silicone polymer compositions that are believed to be suitable and which are comprised of vinyl containing diorganopolysiloxane (corresponding to component B), silicon hydride siloxane (corresponding to component A) and an effective amount of a catalyst which is a halogenated tetrameric platinum complex.

U.S. Patent No. 4,442,060 discloses a mixture of 100 parts by weight of a viscous diorganopolysiloxane oil, 10 to 75 parts by weight of finely divided reinforcing silica, 1 to 20 parts by weight of a structuring inhibitor, and 0.1 to 4 parts by weight of 2,4-dichlorobenzoyl peroxide cross-linking agent.

Silicone resin compositions shown in Table I below have all been used in the practice of this invention. Such compositions of Table I are believed to

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involve formulations that are of the type hereinabove characterized.

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Table I

Illustrative Starting Silicone Polymer Compositions

	<u>Manufacturer</u>	<u>Trade Designation</u>	<u>Components</u> ⁽¹⁾
5	Mobay	Silopren® LSR 2530	Vinyl-terminated polydimethyl/siloxane with fumed silica, methylhydrogen polysiloxane
10	Mobay	Silopren® LSR 2540/01	
15	Dow Corning	Silastic® 595 LSR	polysiloxane
	General Electric	SLE 5100	polysiloxane
20	General Electric	SLE 5106	siloxane resin solution
	General Electric	SLE 5300	polysiloxane
25	General Electric	SLE 5500	polysiloxane
30	Shin-Etsu	KE 1917	
	Shin-Etsu	DI 1940-30	
35	SWS Silicones Corporation	Liquid Rubber BC-10	silicone fluid with silicone dioxide filler and curing agents

Table I footnote:

(1) Identified components do not represent complete composition of the individual products shown.

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When a polymer composition of a silicone polymer and a benzophenone is impregnated into a porous substrate as taught herein, protection of such substrate against ultraviolet radiation is improved, and the degradation effects upon such substrate associated with ultraviolet light exposure are inhibited, as may be expected from prior art teachings concerning the behavior of benzophenones.

Surprisingly and unexpectedly, however, silicone polymer compositions such as used in this invention that contain a benzophenone are believed to display improved viscosity characteristics, particularly thixotropic characteristics as when such a composition is subjected to high shear forces such as are experienced, for example, when a silicone polymer composition is used in the practice of the process described and taught herein.

The normal (ambient conditions or rest) viscosity and rheology characteristics of a liquid silicone polymer composition containing substituted benzophenone of this invention are believed to be lowered by high pressure (shear) forces applied thereto, such as the shear forces that occur during pressured impregnation as taught herein. However, this pressure- and temperature-induced lower viscosity does not reach inoperative or harmful levels, such as hereinabove discussed.

A presently preferred benzophenone additive for use in this invention is 2,4-dihydroxybenzophenone.

The regulation of internal and external rheology, and of viscosity, achieved in a characteristically highly viscous polymer composition of the invention is believed to be an important and desirable feature of the benzophenone and liquid

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silicone polymer compositions which find use in substrate manufacture as taught herein.

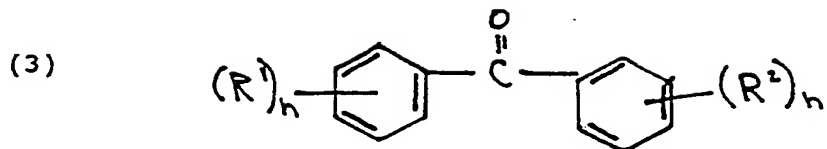
In such compositions of the present invention, a control of compositional rheology, and particularly of complex viscosity, is believed to be accomplishable, if desired, by the selective addition of diluent and additives. These viscous polymer compositions characteristically performance curves indicating substantially level and constant loss modulus, storage modulus, and complex viscosity over extended temperature ranges. The graphic plots of loss modulus, storage modulus, and complex viscosity versus temperature all are believed to characteristically exhibit a sharp knee that shows the moduli to increase in value rapidly at cure temperatures.

Compositions of this invention are controllably curable into polymeric materials which are not sticky or tacky, and which have desirable elastomeric, flexural, strength and resiliency characteristics.

To prepare a silicone polymer composition which incorporates a benzophenone, one preferably admixes the benzophenone with the silicone polymer composition at the time of use. The benzophenone component can be regarded as, or identified herein for convenience as, component (vi). On the same parts by weight basis above used, a composition of this invention preferably contains from about 0.3 to about 10 parts of such component (vi), although larger and smaller amounts can be used, if desired, without departing from the spirit and scope of the invention.

One class of derivatized benzophenones useful in the practice of this invention is characterized by the generic formula:

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where:

R¹ and R² are each selected from the group
consisting of hydroxyl, lower alkoxy, and hydrogen, and
n and m are each an integer of 1 or 2

10 Examples of substituted benzophenones of
formula (3) include

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Table II

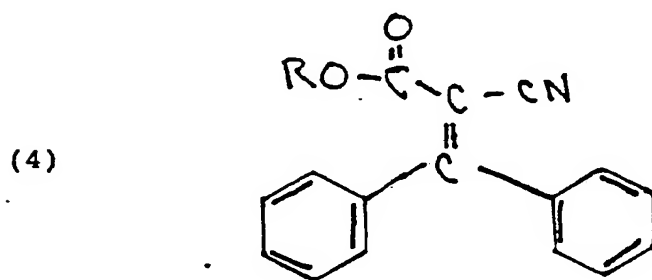
Substituted Benzophenones

5	ID No.	(Name)	(Commercially available under specified trademark from BASF)
	1	2,4-dihydroxybenzophenone	"Uvinul" 400 ¹
10	2	2-hydroxy-4-methoxy- benzophenone	"Uvinul" M-40
	3	2,2', 4,4'- tetrahydroxybenzophenone	"Uvinul" D-50
15	4	2,2'-dihydroxy-4,4'- dimethoxybenzophenone	"Uvinul" D-49
	5	mixed tetra-substituted benzophenones	"Uvinul" 49D

Table II footnote:

(1) Presently most desired substituted
benzophenone

Another class of derivatized benzophenones
useful in the practice of this invention is
characterized by the generic formula:



where:

R^3 is a lower alkyl radical.

An example of a substituted benzophenone of
formula (4) is: 2-ethylhexyl-2-cyano-3,3-
diphenylacrylate (available from BASF under the
trademark "Uvinul N-539").

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In the preceding formulas (3) and (4), the term "lower" has reference to a radical containing less than about 8 carbon atoms.

The contact angle exhibited by a silicone impregnant composition of this invention varies with the particular substrate which is to be saturated therewith. However, the contact angle of water is generally lower for the non-impregnated side than the impregnated side. The combination of the treated substrate, the silicone polymer and the fluorochemical generally produce higher water contact angles than substrates treated only with fluorochemicals. The performance of an impregnant composition may be determined by the nature of a previously applied saturant such as a fluorochemical. Additional suitable starting compositions include 100% liquid curable silicone rubber compositions, such as SLE5600 A/B from General Electric, Mobay LSR 2580A/B, Dow Corning "Silastic® 595 LSR" and "Silastic® 590" which when formulated with substituted benzophenones as taught herein will form a contact angle of much greater than 70 degrees, and typically of 90+ degrees, with typical porous substrates that have a residue of fluorochemical upon (and within) the substrate from a prior saturation.

The silicone polymer composition of this invention can also carry additives into the three-dimensional structure of the substrate during the pressured impregnation. Further, it is preferable, that any additives be bound into the cured composition permanently as located in the three-dimensional structure of the substrate.

Control of the pressurized impregnation step can be provided at a number of areas since the impregnation is sensitive to the viscosity of the impregnant both at atmospheric pressure and at

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superatmospheric pressure. The ambient temperature affecting the impregnant as it is applied, and the pressure-induced temperature changes occurring during application of the impregnant also play roles in viscosity and therefore the shear process. Of course, the chemical composition of the silicone polymer impregnant composition of this invention also plays a role in the shear process and assists in assuring that the treated substrate passageways are encapsulated and the cells remain open but lined.

The amount of silicone polymer impregnant utilized and the weight add-on thereof are again variable and dependent upon several things such as the treated substrate, the desired end use of the substrate, cost and the like. Broadly, substrate weight add-ons can be as little as about 5 up to about 200 weight percent of the untreated substrate. For producing breathable, water-repellant substrates of this invention, weight add-ons are preferably in the range of about 10 to about 100 weight percent, of the untreated substrate weight.

The fluorochemical saturant composition may also contain a bonding agent. The bonding agent can facilitate the bonding of the water repellent chemical and/or the impregnate to the three-dimensional structure of the substrate within which it is saturated. Mobay Silopren® bonding agent type LSR Z 3042 and Norsil™ 815 primer are representative compositions that can be used to facilitate bonding of the water repellent chemicals and/or impregnant to and within the substrate. Use of the bonding agents is not essential to the practice of this invention, but may improve bonding of the fluorochemical and/or the silicone polymer composition to the cellular or porous matrix of the substrate.

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The fluorochemical particularly, and also the bonding agents when used, are preferably affixed to the three-dimensional structure of the substrate prior to a subsequent pressured impregnation. Complete affixing is not necessary for the fluorochemical. The fluorochemical will apparently facilitate the pressured impregnation of a silicone polymer composition even if the fluorochemical is not preliminarily fixed within or located within the substrate being treated. However, fixing, especially by sintering, causes the water repellant chemicals to flow and to become better attached to the three-dimensional structure of the substrate. In this regard, a lesser amount of fluorochemical will remain in place better, and will better facilitate the subsequent pressured impregnation of the silicone polymer, if the sintering or insolubilizing step is performed prior to a pressured impregnation.

After a fluorochemical saturation followed by a silicone polymer impregnation and curing, a substrate may have a surface contact angle of greater than about 70 degrees, and more typically greater than about 90 degrees. Substrate impregnation pressures can involve transverse force or pressure in the range of tens to hundreds of pounds per square inch of substrate surface.

Similar to the functional qualifications achieved by the use of a fluorochemical in the preferred saturating pretreatment step, the silicone polymer impregnant introduced by the pressured impregnation step can be defined by its functional qualifications. For example, the silicone polymer impregnant produces a contact angle with a fluorochemical treated substrate of greater than about 70 degrees. In measuring the liquid contact angle with a fluorochemical treated surface and a silicone treated surface, it will be understood that

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such a contact angle cannot exceed 180 degrees. The contact angle of a fluorochemical will be within a range of about 90 degrees to about 180 degrees while the contact angle of the silicone polymer will be within a range of about 70 degrees to about 180 degrees.

The contact angle exhibited by the silicone polymer impregnant can be, if desired, qualified against the particular substrate saturated with the particular fluorochemical saturant. The selection of a suitable silicone polymer composition may be determined by the nature of the previously applied fluorochemical saturant. The fluorochemical saturant and silicone polymer compositions are, however, not critical to the practice of this invention since wide respective compositional ranges may be involved. In particular, a substantially undiluted liquid silicone rubber which is available from suppliers such as GE, Dow Corning, and Mobay-Bayer will characteristically form a contact angle of much greater than about 70 degrees, and typically greater than about 90 degrees, with typical porous substrates that have a residue of fluorochemical upon (and within) the substrate resulting from a prior saturation.

The silicone polymer composition can carry additives into the three-dimensional structure of the substrate the pressured impregnation step of the method of the invention. Further, the silicone polymer composition, when cured, is capable of adhering to fibers, and other additives dispersed therein. Thus, additives are positioned adjacent to or on surface of the matrix, fibers and the like, in a position where they can be beneficial.

Examples of additives that are dispersible in effective amounts in a viscous silicone polymer composition typically at a concentration of about 0.1 to

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20 weight percent (based on total composition weight) include ultraviolet absorbers, flame retardants, aluminum hydroxide, filling agents, blood repellents, flattening agents, optical reflective agent, hand altering agents, biocompatible proteins, hydrolyzed silk, and the like. Hydrolyzed silk is a texturing agent that imparts a substantially silky feel to a substrate treated in accordance with the method of the invention regardless of whether or not such substrate surface is itself silk.

Examples of other silicone polymer dispersible agents include those affecting thermal conductivity, radiation reflectivity, electrical conductivity, and other properties. For example, if a metallic sheen and/or thermal or electrical conductivity or infrared background blending is desired, powdered metals may be dispersed therein.

The impregnation is sensitive to the viscosity of the silicone polymer composition. The impregnation temperature affects the silicone polymer composition by reducing or altering its viscosity. Shear-induced temperature changes occurring during application or during subsequent shear processing of the silicone polymer can affect viscosity. The chemical composition of the silicone polymer also plays a role in the treating process and the product and can assist in the regulation of the filling of open cells.

Various machines and procedures can be used for performing the process of the invention. Illustrative machines and processes of use are now described which are suitable for use in the practice of this invention.

An embodiment of a machine suitable for accomplishing pressured impregnation in accordance with this invention is illustrated in side elevational view

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in Figure 4a. Two blades 200 and 210 in opposed relationship to one another are provided in functional combination with means for providing a precisely adjustable gap therebetween through which a substrate 300 is drawn while having a silicone polymer composition 220 applied to either one or both surfaces thereof. An enlarged side view of a typical blade 200 or 210 is shown in Figure 4b. Dimensions A, B, C, D, and E are typically and exemplarily illustrated as, respectively, about 3-1/2 inches, about 1-1/2 inches, about 2 inches, about 1/2 inch, and about 5/16 inch. The narrow edge is preferably milled to a tolerance of about 1/10,000 inch continuously along the edge surface of each blade which is typically and illustratively about 38 inches long. Each of the corners of the narrow edge is preferably and illustratively a hard (not beveled or ground) angular edge. Each blade 200 or 210 is typically and illustratively made from carbon steel or stainless steel. A reservoir of silicone polymer composition is formed preferably on one upper surface of the substrate 300 behind (relative to the direction of substrate movement) an upper one of the blades 200 and 210 which are mounted on a frame (not shown) so as to extend horizontally. As the substrate 300 is drawn through the slit orifice defined between blades 200 and 210, some impregnant becomes entrained on the substrate surface and moves through such slit orifice, thereby accomplishing pressurized impregnation of substrate 300. The slit orifice gap is chosen preferably and illustratively to be slightly smaller than the relaxed thickness of the starting substrate.

Referring to Fig. 4a, a second pressured impregnation station is seen to be positioned downstream (relative to the direction of substrate movement) from the pair of opposed blades 200 and 210. At this

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station, a knife blade 230 is provided which has an edge that presses against the substrate 300 to reintroduce the silicone polymer composition into the substrate 300. One side of blade 230 adjacent the edge thereof is
5 strongly biased against an adjacent cylinder or bar 240, which, in the embodiment shown, does not rotate. If desired, bar 240 can be journaled for rotational movement. As the substrate is moved between the blade 230 and the bar 240, it is preferably uniformly
10 compressed. Preferably, the compression force is in the range of about 10 to about 500 inch pounds, although higher and lower forces can be employed. As the substrate 300 passes over the edge of blade 230, it is drawn away at an angle from the blade edge under
15 longitudinal tension. For example, longitudinal tension in the range of from about 0.5 to 10 pounds per inch can be employed. Such pressured impregnation serves to distribute and reintroduce the polymer composition in the substrate. Excess polymer composition is removed by
20 blade scraping. Passage of the substrate 300 between the blade 230 and the bar 240 and over the edge of the blade 230 is believed to produce shear forces in the impregnant 220 (within the substrate 300) that facilitate flow and distribution thereof within the
25 three-dimensional matrix of the substrate 300. Concurrently, blade 230 also scrapes excess silicone polymer composition impregnant off the substrate's surface in contact with the edge of blade 230.

Both the steps of fluorochemical saturation
30 and of subsequent silicone polymer composition impregnation are performable, if desired, in production volumes, and at speeds which can be typical of the so called high end range of fabric finishing lines. The fluorochemical saturation is conveniently accomplished
35 conventionally by using a padbath in which the substrate

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is run through a dilute treating bath followed by squeeze rollers to remove excess liquid and overdrying. In general, any method of applying the fluorochemical would be acceptable.

5 Another embodiment of a machine suitable for accomplishing pressurized impregnation in accordance with this invention is shown diagrammatically in Fig. 5 which also illustrates a process embodiment of this invention. At an impregnation head, a pressurized
10 introduction of the silicone polymer composition into the substrate is first carried out. At a subsequent stage, a controlled pressure reintroduction, distribution, and metering of the silicone polymer impregnant and a recovery of excess liquid impregnant
15 transpires using a shear knife or blade which applies transverse force against the impregnated substrate laterally across the substrate. In a subsequent stage, further controlled pressure reintroduction and metering takes place by means of a flexible blade, such as a so-
20 called flex-knife or Spanish knife. Here, additional recovery of excess impregnant is accomplished. In all knife-applying states, the excess impregnant removed is collected and preferably passed by a recycling system back to the initial, pressured introduction stage to
25 achieve process operating economies. Still further successive impregnant pressure reintroduction stages may be used if desired. The direction of the arrows in the diagrammatic representation of Fig. 5 shows the general direction of movements in the region of the impregnation
30 head, including the general direction of impregnant movement in the practice of such process.

The apparatus employed in the present invention functions first to apply and preferably concurrently impregnate a silicone polymer composition
35 into a substrate under pressure. Such silicone polymer

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composition is then reintroduced, distributed, and metered in a controlled manner in the treated substrate with the aid of transversely applied shearing force and compressive force such that the impregnated composition becomes distributed in the substrate so that the passageways through the substrate matrix are at least partially encapsulated while the open cells are lined with, and not completely filled by the silicone polymer composition. During treatment, the substrate is longitudinally tensioned and the pressurized application and impregnation and the subsequent shearing and compressive actions are successively accomplished in localized zones preferably extending generally laterally across the substrate (that is, generally perpendicularly to the direction of such longitudinal substrate tensioning) using transversely applied force exerted locally against surface portions of the substrate during each impregnation and shearing operation. The substrate is conveniently and preferably, but not necessarily, moved longitudinally relative to such laterally extending substrate processing zones. The impregnation, shearing and compressing steps are preferably carried out successively or sequentially. Such zones are themselves preferably at stationary locations while the substrate is moved, but if desired, the substrate can be stationary while the zones are moved, or both. The result is that the silicone polymer composition impregnant flows into the substrate and is distributed therethrough generally uniformly to a predeterminable and controllable extent.

A schematic side elevational view of another embodiment of a suitable pressurized impregnation machine for use in the practice of the invention is shown in Figure 6. This machine continuously moves a longitudinally tensioned substrate 60 successively

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through a pressure impregnation station which incorporates a reverse roll coater having rollers 10 and 11, a shear station which incorporates a shear knife 20, and a finishing station which employs at least one so called flex-knife (or Spanish knife) 30. Optionally, but preferably (for reasons of process operating economics) excess silicone polymer composition that is removed from substrate surfaces in the shear station and finishing station is returned to the pressure impregnation station for reuse using liquid recovery and recycle system 40. In the pressure impregnation station, a silicone polymer impregnant 50 is contained within reservoir 51. Roller 12 rotates in the indicated direction so that its circumferential surface, preferably a textured or gravure surface, picks up liquid 50 from reservoir 51 and deposits it on the circumferential surface of roller 10 across a controlled width gap 13 between rollers 10 and 12. Typically, gap 13 is actually less than the unencumbered thickness of the starting substrate 60. Roller 10 also preferably has smooth, highly polished chrome or stainless steel finish and has a circumference that is machined to a tolerance of 1/10,000 inch. A textured or gravure surface may also be used. Roller 10, rotating in the roller arrow indicated direction, which is opposite to the direction of travel of substrate 60, applies the impregnant to one surface of the moving substrate 60. Roller 11 is urged with a compressive force against the back or opposed surface of substrate 60 and roller 11 rotates in a direction which is the same as that in which substrate 60 travels. Roller 11 aids in achieving the desired pressured impregnation of substrate 60 by the silicone polymer impregnant from the surface of roller 10.

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Referring to Figure 6, the impregnant is believed to be introduced into the substrate 60 by the aid of a back-pulling or shearing action resulting from the distorting and pressuring of substrate 60 caused by rollers 10 and 11 rotating in the same direction. This direction may be the indicated direction with roller 10 rotating against the linear movement of substrate 60 indicated by directional arrow 61, or all rollers 10, 11 and 12 may be reversed in respective rotational direction so as to cause each roll to turn in an opposite direction relative to that direction which is illustrated by the respective roller arrows in Fig. 6. Regardless of which side of substrate 60 is back-pulled or subjected to shearing action by a reverse rotating roller, the substrate 60 is stretched and distorted to pull open the cells of the substrate 60 and to aid in impregnating substrate 60 with impregnant 50. This distorting, and particularly this stretching, is believed to facilitate the full and deep introduction of the impregnating liquid into the moving substrate 60.

The extent of pressured impregnation of the silicone polymer impregnant 50 into the substrate 60 which occurs between rotating rollers 10 and 11 is controllable to some extent by such variables as the speed of roller rotation, the pressure exerted by rollers 10 and 11 on substrate 60, the durometer hardness and surface characteristics of each roll 10 and 11. However, the pressurized impregnation may also be carried out with rollers 10 and 11 which have finely milled, smooth circumferential surfaces. The viscosity of impregnant 50 and the amount of impregnant 50 transferred from roll 12 to roll 10 across gap 13 may also be varied to regulate impregnation. Feed roller 12 preferably rotates counter to application roller 10. The impregnant 50 can be monitored to assure that its

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homogeneous composition is maintained. If desired, the impregnant 50 formulation can be altered to adjust to process needs during a continuous treating operation.

The result of the pressured substrate 60 impregnation which is accomplished between rollers 10 and 11 using a silicone polymer composition impregnant 50, which can have the viscosity or consistency of a conventional bathtub caulk composition, is to produce a substrate 60 whose open cells can be substantially completely filled with such impregnant. In, for example, the case of a synthetic leather, the impregnation can be such that many spaces (or open cells) of the synthetic leather are filled with impregnant 50. However, the amount of impregnant 50 which is introduced into substrate 60 can be much less than such a saturation level; for example, the amount introduced can be insufficient even to coat or line completely all the open cells of the substrate. Actually, the impregnant 50 can be relatively non-uniformly distributed in the substrate after such pressurized impregnation. The action of the shear knife 20 in the next zone of processing is such as to smooth out and to make uniform the distribution of impregnant 50 in substrate 60. Also, the shear knife 20 helps regulate the amount of impregnant 50 that is allowed to remain in substrate 60.

After the shear zone, if desired, a top coat polymer can additionally be introduced; for example, just before or after flex knife 30. By overcoating, for example, the original impregnant with a dilute or very thin second or top coat, a more tightly cross linked impregnated or encapsulated product may be achieved, or surface properties of the product can be varied or improved. For example, the top coating can comprise a dilute dispersion of a fluorochemical composition. In a

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substrate treated therewith, such treatment enhances surface properties of the substrate, such as by increasing grease or chemical penetration resistance, or soil resistance, or the like. The dilute fluorochemical dispersion can be applied by spraying, misting, or the like. Both treating agents then enter a curing stage, which can be accomplished conveniently by passing the treated substrate through an oven wherein the temperature and substrate residence time are sufficient to cure both the fluorochemical and silicone polymer impregnants to a desired extent, or by radiation, if desired.

The amount of silicone polymer impregnant actually introduced through the pressured impregnation, and into the preferably stretched openings of the open cells of the substrate 60 is influenced by such factors as the velocity of movement of substrate 60, the viscosity characteristics of impregnant 50, the compressive pressure exerted by roll 10 against roll 11, by the longitudinal tension exerted upon the tensioned substrate 60, the impregnant distribution achieved by shear blade 20 and scraper flex knife(s) 30, and the like. In particular, the impregnant reintroduction and distribution believed to be achieved by bar or shear knife 20 is achieved by the exertion of a pressure against moving tensioned substrate 60. The shear force and the temperature elevation due to such shear force results in the impregnant 50 flowing upon the three dimensional structure of the substrate 60 and the knife 20.

Preferably, the impregnant 50 is thixotropic. The flowing of the impregnant 50 into the substrate 60 using controlled liquid rheology preferably does not result at the time of impregnation in a fluid viscosity which is so low as to cause the impregnant to spread

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into and be distributed substantially uncontrolled throughout the substrate 60. However, the flowing activity of the viscous impregnant is preferably accomplished using an impregnant 50 which has a

5 controllable rheology and viscosity such that impregnant 50 will achieve a desired encapsulation of the passageways of the matrix of the substrate 60.

A plurality of substrate tension control devices 70 can be used in the region of metering bar or

10 shear knife 20 and in the region of reintroduction scraper flex knives 30 along substrate 60 in order to provide the capacity for precision control of the tension exerted on substrate 60 and of the compressive pressures and shear forces exerted on substrate 60 at

15 metering bar or shear knife 20 and flexible knives 30.

As shown in Figure 6, the machine preferably includes an impregnant 50 recovery and recycling system which more preferably also includes a filtering subsystem, such system being diagrammatically

20 represented and indicated by dashed line path 40. This system includes a collection tray, or pan, 41, positioned under and behind the moving substrate 60 to collect along the sides of substrate 60, the excess impregnating liquid as it is wiped off from the

25 substrate surface contacted by the metering bar 20 and/or by the recovery knives 30 and passed laterally into pan or tray 41. From the recovery collection tray 41, the excess impregnating liquid 50 is pumped back through filter 42 into the reservoir 51 of the reverse

30 roll coater for loading and distribution on the surface of roller 12, transfer to roller 10, and reapplication to portions of continuously moving substrate 60. The ability to reuse the excess impregnant 50 wiped from the moving substrate 60 rather than losing such impregnant

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within the process makes the entire process more economically attractive.

Another embodiment of a machine suitable for use in the practice of this invention is shown schematically in side elevation in Fig. 7. In this embodiment, rollers 10 and 11 of the Fig. 6 apparatus are replaced with a combination of a reservoir 67, and a bar or shear knife 100. The reintroduction bar or shear knife 100 pressurizes the impregnant liquid 66 that is applied or deposited onto the moving substrate 60 from the reservoir 67 as a liquid or bath. The substrate 60 in effect constitutes a retaining wall for a part of the reservoir 67. The reservoir 67 thus functions to hold a pool of the silicone polymer impregnant 66 against a surface of the moving substrate 60 which in the embodiment shown, is moving vertically upwardly. The bar or shear knife 100 functions to apply pressure or force upon the silicone polymer impregnant 66 that was deposited on the substrate 60, to cause the impregnant 66 to penetrate the substrate 60. The knife 100 also serves to distribute and move the impregnant in the substrate 60 and to accomplish encapsulation of the passageways of the substrate matrix or lining of the cell or pore walls thereof. Excess impregnant 66 is also scraped away by knife 100. Optionally, one or more of flex knives 110 function to further reintroduce, distribute the impregnant 66 and to encapsulate the passageways of the matrix of substrate 60 and line wall portions of open cells or pores thereof. The knives 110 can be considered to function in a manner which is equivalent to the knives 30 on the treated surface of substrate 60 in the Fig. 6 apparatus.

Typically, any impregnant scraped from the moving substrate 60 by bar knife 100 falls directly back into the reservoir 67. Impregnant scraped from the

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moving substrate 60 by scraper knife 110 is collected in sloping trough 120 and returned by falling along the indicated dotted line path to the reservoir 67.

Longitudinal tension control of the moving substrate 60 is regulated by tension control devices 70 (as in the Fig. 6 embodiment) from a region beginning after reservoir 67 and extending to an oven 80 along the path of substrate 60 travel.

Relative to the Fig. 7 embodiment, the Fig. 6 embodiment is believed to exhibit a wider degree of control in the practice of the present impregnation process. Particularly, both the initial applied amount, and also the successive pressurings of, a silicone polymer impregnant 50 are precisely controllable.

Relative to the Fig. 6 embodiment, the Fig. 7 embodiment is characterized by the capability for operation at higher substrate 60 transport speeds, typically at speeds characteristic of higher end commercial fabric finishing line operations. The embodiment shown in Fig. 6 is believed to be suitable for producing open cell or pore wall lined substrates when the substrates are of the thicknesses characteristic of garments, leather or the like, and where deeply controlled pressured impregnation over distances extending perpendicularly into and through a substrate greater than about 1/16 inch is not generally required.

Because of the discontinuous nature of a natural leather sample, the application procedures for the above embodiments will need to be further modified. This can be accomplished by mounting the material on a continuous supporting platform and moving the entire platform under the reverse roll coater, shearing stations and finally through the curing oven.

Illustrative parameters of the adjustments of the first embodiment of the apparatus shown in Figure 6,

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are contained within the following three Tables III, IV and V. The first column of each Table lists a parameter that is adjustable. For Table III, these parameters concern top roller 10 shown in Fig. 6. For Table IV, these parameters concern reintroduction metering bar or shear knife 20 shown in Fig. 6. For Table V, these parameters concern tensioning devices 70. The second column of each Table indicates the typical respective ranges of parameter adjustment. The third column of each Table indicates the effect of such adjustments on substrate impregnation.

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TABLE III

MACHINE ELEMENT PARAMETERS

First Stage Introduction Pressure Rollers:

	<u>Top Roller Adjustment Parameters</u>	<u>Variability to Adjustment</u>	<u>Effect of Adjustment of</u>
10	Top roller pressure down and in at an angle or in front of roller	0 to 500 lbs/ linear inch	Delivery quantity, depth, residue presence
	Top roller surface	Smooth to highly textured	Degree of agitation and distortion or friction action
15	Top roller speed	50 to 1,000 RPM	Varies quantity by varying speed and distortion independent of substrate speed in relation to second and third stage systems
20	Metered Film Thickness on top roller	.05 mil thick non-contiguous film to 10 mil on roller	Contiguous film delivery quantity controlling thicker film presence and allows more impregnant to dam at either second or third stage
25	Lower roller surface and composition	Low durometer material surface to high strength metals	Low durometer material allows pressure from upper roller to be agitation of yarn bundles or filament's metal surface causes more complete distortion and agitation of yarn and fiber/filament

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TABLE IV

MACHINE ELEMENT PARAMETERS

Second Stage Reintroduction Bar Knife:

	<u>Adjustment Parameters</u>	<u>Variability to Adjustment</u>	<u>Effect of Adjustment of Substrate</u>
10	Angle of bar knife	Bar knife faces forward to meet substrate coming to bar; bar knife to substrate, bar faces away or racked back from substrate run direction	Angle effects shear forces on impregnate and determines distortion or vertical agitation as it relates to causing flow of impregnate; can determine reintroduction of impregnate by dammed quantity of impregnate
15	Edge Shape	Knife very sharp	Sharpness of knife affects shear forces. The sharper and thinner the edge, the greater the shear forces at the contact edge
20	Pressure	Relates to tautness	Greater pressure increases forces at contact edge

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TABLE V

MACHINE ELEMENT PARAMETERS

I. Second Stage Bars Below :

	<u>Adjustment Parameters</u>	<u>Variability to Adjustment</u>	<u>Effect of Adjustment of Substrate</u>
10	Substrate Speed	Range of machine speed possible	Affects the shear forces at contact edge above, where impregnant is being forced into the substrate
15	Pressure on substrate	Range of motion of bar	Tightens or loosens tension on substrate which in turn affects shear forces at contact edge

II. Third Stage Reintroduction Flex Knife:

	<u>Adjustment Parameters</u>	<u>Variability to Adjustment</u>	<u>Effect of Adjustment of Substrate</u>
20	Recovery system		Filters and pumps deliver impregnant back to first introduction stage

25 A schematic, side elevational view of another suitable pressurized impregnation system or apparatus 73 for practicing the present invention is shown in Fig. 12a. In this apparatus, a continuous substrate 74 is moved along a substrate pathway from a supply roll 76 to a take-up roll 77.

30 In a first functional processing station 78, a silicone polymer composition is applied to one face (here, the upper face 79) of substrate 74 by a conventional reverse roll coater apparatus 81 wherein such composition is applied to the surface of a reversely rotating (relative to the direction of travel of substrate 74) coating roll 82 from a nip region

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reservoir 83 formed between the coating roll 82 and a transfer roll 84 (which rotates in the direction of travel for substrate 74 but whose surface does not contact substrate 74). The substrate 74 is transversely compressed between coating roll 82 and drive roll 86 as it passes through station 78. Thus, polymer composition is applied under a positive pressure against face 79 by coating roll 82 which functions to cause the composition to be impregnated into substrate 74. A present preference is to use a coating roll 82 which has smooth chrome plated surfaces.

Largely for purposes of controlling the alignment of substrate 74 with rolls 82 and 86, the substrate 74 is pretensioned by coacting clutching rolls 87, 88 and 89. After it passes over guide roller 91 on the substrate pathway from supply roll 76, the substrate 74 passes over roll 87, between rolls 87 and 88, around roll 88, and between rolls 88 and 89. The clutching rolls 87, 88 and 89 are components of a conventional clutching mechanism (not detailed) which provides for adjustments between rolls 87, 88 and 89 so that selective tensioning of substrate 74 is achieved along the substrate pathway between the clutching rolls 87, 88 and 89 and the nip region 92 defined between rolls 82 and 86 with the intervening roller roll 93 being used for guidance of substrate 74. The clutching rollers 87, 88 and 89 also function to smooth out and extend substrate 74 before it enters the coater apparatus 81 so that in the apparatus 81, the substrate will have polymer composition uniformly applied thereto.

After passing nip region 92 the substrate 74 is preferably highly longitudinally tensioned along the substrate pathway extending from nip region 92 to compensating and regulating coacting tension rollers 94, 95 and 96. The tension rollers 94, 95 and 96 are

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components of a conventional web tension adjusting and regulating mechanism (not detailed) which provides for on-line, in-stream operator controlled adjustments between rollers 94, 95 and 96 that permit selective control of the tautness of substrate 74 particularly in the substrate pathway region from nip region 92 to rollers 94, 95 and 96.

Along the tensioned substrate pathway region, the substrate 74 successively passes through each one of a series of processing stations 98, 99 and 100.

At each of the stations 98 and 99, a substantially non-flexible shear knife 101 and 102, respectively, extends laterally across substrate 74 with the substrate 74 being entirely unsupported on the lower face 101 thereof which is opposed to upper face 79 and to the respective blades of each shear knife 101 and 102. Both to control the amount and type of shear force independently applied by each knife 101 and 102 the substrate 74 passes over each knife edge in a contacting relationship and three idler rolls 105, 106 and 107 that are provided in a typically fixed (but off-line adjustable) relationship relative to knives 101 and 102 as apparatus 73 is operated.

Relative to the direction of substrate 74 travel, idler rolls 105 and 106 thus are positioned so that roll 105 is on the lead side, and roll 106 on the trailing side, of knife 101 while idler rolls 106 and 107 are positioned so that roll 106 is on the lead side, and roll 107 is on the trailing side of knife 102. The angle of inclination or tilt of each blade 101 and 102 relative to the vertical is adjustable over a wide range, but it is presently preferred to adjust the blade inclination angle for each blade between about $\pm 45^\circ$ relative to the vertical with the substrate 74 being horizontal. In the apparatus embodiment 73 shown, each

-74-

respective blade is functionally associated with a knife back support 108 and 109, respectively. Each support 108 and 109 permits its associated blade 101 and 102 to be adjustably inclined in relation to the vertical relative to a supporting frame (not shown).

Another adjustable variable is the amount of angular substrate depression which, in the embodiment shown, extends downwardly, achieved by substrate 74 in its passage over the circumferential edges of adjacent rolls 105 and 106 relative to knife 101, and in its passage over the circumferential edges of rolls 106 and 107 relative to knife 102. Considering the place where the knife 101 or knife 102 contacts the substrate 74 to be a hypothetical point, the angle of the knife 101 or knife 102 relative to the substrate can be in the range of about 30° to about 140°.

While it is presently preferred to employ shear knives 101 and 102 which have straight edges, it will be appreciated that shear knives having somewhat curved edges can be used, if desired. For example, when treating a substrate which displays differential longitudinal stretch characteristics laterally thereacross in response to a uniformly laterally applied longitudinal tension, it appears to be possible to laterally equalize laterally the shear forces applied to a substrate by employing a suitably curved shear knife which appears to compensate for such a differential stretch characteristic.

While it is presently preferred to employ shear knives 101 and 102 which have sharp edges, more preferably edges which are sharpened to a micro edge uniformity of at least about root mean square (RMS) 8.

While it is presently preferred to employ shear knives 101 and 102 which are formed of steel, other materials of knife construction could be used if

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desired, such as metal alloys, non-metallic composites, and the like.

Those skilled in the art will appreciate that the amount of shear force applied by a shear knife 101 or 102 transversely against a substrate 74 is a function of many variables, with probably the most important or principal variables being the fluorochemical pretreatment, the silicone polymer viscosity and the longitudinal substrate tension (assuming a fixed spatial position for idler rolls 105, 106 and 107 and shear knives 101 and 102 during operation).

When a suitable and preferred level of applied shear force and substrate tensioning has been achieved to produce a product having lined cell or pore walls and encapsulated passageways in its matrix, one can usually hear a distinctive sound in the region of a shear blade 101 and 102. This sound can also be heard in the vicinity of shear blades being used in the operation of other processes described herein. This sound can in fact be used by an operator as a rough guide as to whether or not he is succeeding in producing a silicone polymer impregnated product containing lined cell walls and encapsulated passageways through its matrix.

Idler roll 105 also functions as a compensator roll for mechanically adjusting and controlling substrate tension after coating apparatus 81 and before knife processing begins. The substrate tension is sensed electronically, and then roll 105 is automatically raised or lowered to achieve substrate tensioning adjustments so as to maintain a preset tension in substrate 74.

After passing over roll 107, the substrate 74 is passed over the circumferential surface of a conventional padder roll 111.

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Between the idler roll 107 and the padder roll 111, a flexible so-called "flex-knife" or "Spanish knife" 100 is positioned. Preferably, the blade of this flexible knife 100 is inclined at an angle with respect to the substrate 74 passing thereagainst so that the knife 112 exerts a compressive force against the face 79 of substrate 74 with opposed face 103 being entirely unsupported. The angle with respect to the web can range from about 60° to about 140° for the adjustment of the inclination angle of the flex knife. To provide adjustability for flexible knife 100, knife 100 is functionally associated with a mounting bracket or back support 113 which in turn is adjustable relative to an apparatus frame (not shown).

The purpose of shear blade is to reduce the viscosity of the silicone and cause it to flow.

The purpose of a flex blade is primarily for smoothing possible impregnate imperfections and smoothing surface residue to form a smooth film on the surface when required.

The flex blade is 22 gauge stainless steel, surfaced to be smooth with no surface imperfections and the edges are milled to have no radius. The 22 gauge steel allows for enough flexibility to smooth the surface and "give" if any surging occurs during tensioning. The shear blade must be completely rigid to prevent vibrations or chattering which will cause uneven silicone distribution and to initiate viscosity reduction.

In the embodiment shown in Fig. 12a, the padder roll 111 is not employed as a substrate 74 treating means.

After leaving the mechanical tension compensator rolls 94, 95 and 96, substrate 74 is under reduced or preferably minimal tension and is led along a

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pathway which extends over spacer rolls 113 and 114. In the region over spacer rolls 113 and 114, and generally between tension roll 96 and idler roll 117, a platform 116 is conveniently positioned which can incorporate suitable instrumentation panels, operating controls and the like so that an operator can observe the operation of the apparatus 73 in the practice of the process of this invention and then control and regulate the same. A position which is suitable for operator observation of a substrate in progress that is located in the vicinity of the tenter frame 118 is desirable because it has been observed that a substrate being processed can experience some distortion owing to the forces exerted thereon. These distortions can be metered and observed and the tenter frame 118 adjusted by the operator so that, as the substrate 74 passes therethrough, the substrate 74 can be straightened or shaped either longitudinally or laterally, as desirable or considered necessary for an individual substrate. If desired, the tenter frame 118 can be automatically operated to apply tensioning forces to a substrate in accordance with a predetermined program, or the like.

The tenter frame 118 also provides the start of a new zone of limited longitudinal and transverse tensioning which extends forwardly along the substrate pathway from tenter frame 118 through oven 119 to a tension compensator, here shown as utilizing three tension rolls 121, 122 and 123 which are part of a conventional mechanical tension compensator subassembly which is similar in structure and function to the compensator subassembly incorporating the previously described tension rolls 94, 95 and 96. The longitudinal tensioning of substrate 74 as it passes through oven 119 is employed to control the substrate 74 as it passes through oven 119 as regards web dimensional limits.

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This tensioning is at a level that does not introduce significant distortion into the substrate, yet substrate sagging is avoided, as from thermal expansion and elongation. Support rollers (not shown) can be used in the oven 119 to avoid sagging and to maintain uniform heat exposure.

In addition to serving as tension regulating means, the rolls 121, 122 and 123 also serve to provide a cooling pathway for the substrate 74 as it emerges from the oven 119 before it passes over guide roller 124 and into take-up roll 77.

The oven 119 functions to cure (as elsewhere described herein) the silicone polymer composition impregnated into substrate 74. Oven 119 can be operated with gas or some other energy source. Oven 119 can extend for from about 12 to 20 yards, a 15 yard long oven being convenient.

Curing temperatures of from about 320° to about 500°F, applied for times of from about 2 minutes to about 30 seconds (depending upon the temperature) are desirable. If a curing accelerator is present in the silicone polymer, curing temperatures can be dropped down to temperatures of about 265°F or even lower (with times remaining in the range indicated).

In place of an oven, or in combination with an oven, a source of radiation can be employed (electron beams, ultraviolet light, or the like) to accomplish curing, if desired.

Less than the full heating capacity of the oven 119 can be used, if desired, or if full oven capacity is not needed, either longitudinally or vertically. For example, only top heating or only bottom heating with respect to the web can sometimes be used as compared to a combination of both top and bottom heating.

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The take-up roll 77 operates at approximately the same speed as the supply roll 76. When the rotational speeds of take-up roll 77 are not synchronized with rotational speeds of the supply roll 76, the tension roll combination of rolls 121, 122 and 123 can be used to take up or reduce substrate slack, as the case may be.

Substrate transport speeds can vary widely; for example, from about 2 yards per minute to about 90 yards per minute.

The process described above can be used in various forms or embodiments. Referring to Figs. 12b and 12c, two alternate variations or modes are seen. In such views, similar components are similarly numbered, but with the addition of single prime marks thereto in the case of Fig. 12b, and double prime marks thereto in the case of Fig. 12c.

In Fig. 12b, a further stage of substrate pressurization is introduced after the flex knife 112' and before the tenter frame 118'. Here, the substrate 74' after passage through the flex knife 112' is passed through the nip region 126 existing between padder roll 111' and associated transfer roll 127 where the substrate 74' is subjected to compression between such rolls 127 and 111' for the purpose of achieving a better distribution of silicone polymer composition on substrate 74'.

After leaving nip region 126, the substrate 74' is retained under some compression against roll 127 by means of retaining bar or roll 128 for similar purposes.

If desired, the roll 128 can be replaced by a flex knife (not shown) over whose edge the substrate 74' passes after departure or preparation from roll 127.

The action of such flex knife on substrate 74' can

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accomplish substantial further polymer distribution in substrate 74'.

Referring to Fig. 12c, there is seen an embodiment where the substrate 74'' is passed through the nip region of rolls 111'' and 127''. Here not only is use of the mechanical tension roll combination having rolls 94, 95 and 96 (as in Fig. 12a) eliminated, but also the rolls 111'' and 127'' serve to end the region of high longitudinal tension in the stages of blade or knife application to substrate 74'' and to provide the desired reduced pressure for substrate passage through a curing station, here illustrated by oven 119'' which succeeds the desirable and preferred intervening tenter 118''.

A presently preferred substrate is one which is both fluorochemical and silicone polymer treated and is breathable, water resistant and rewashable. The substrate is characterized as being a longitudinally tensionable porous substrate having opposed, substantially parallel surfaces that are comprised of a matrix having open cells or pores. The substrate is substantially uniformly impregnated with a fluorochemical and thereafter impregnated with a silicone polymer composition. The polymer composition has a thickness in the range of about 0.01 to about 50 microns. At least one surface thereof is characterized by having a visual appearance which is substantially the same as the visual appearance of one surface of the starting porous fibrous substrate. The substrate is further characterized by containing from about 5 to about 200 weight percent of the untreated substrate of silicone polymer composition. More preferably, such a substrate is a porous synthetic leather comprised of synthetic polymer or natural material, or mixtures thereof.

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When such a substrate has fibers, such fibers are presently comprised of a synthetic polymer, preferably selected from the group consisting of polyamides, polyesters, regenerated cellulose, cellulose acetate, and mixtures thereof.

Preferred substrates of this invention are more specifically characterized by having a water drop contact angle in the range of about 90° to about 160°; a rewash capability of at least about 3; a breathability of at least about 35% of untreated substrate; and a water repellency rating of at least about 80 prior to washing.

A general process for making a porous substrate of this invention comprises the steps of: tensioning a starting flexible, porous substrate as above characterized, applying a curable silicone polymer composition having a viscosity sufficient to line the walls of the cells or pores of the substrate to at least one substrate surface, and then moving over and against the surface a uniformly applied localized shear force of the substrate while tensioned to distribute said composition within said substrate generally uniformly and at least partially individually encapsulate at least some of the passageways of the substrate matrix with the silicone polymer composition and at least partially individually line surface portions of at least some walls of cells or pores with said composition, and leave at least some of said cells unplugged. Thereafter, the substrate is subjected to conditions sufficient to cure the composition in the substrate. Curing is accomplished by heat, radiation, or both.

A presently preferred process for making a fluorochemical and silicone resin treated substrate having breathability, water resistance and rewashability which is adapted for continuous operation comprises the

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successive steps of: impregnating a flexible porous substrate having open cells with a fluorochemical, tensioning the fluorochemical impregnated substrate while sequentially first applying to one surface thereof a curable silicone polymer composition and concurrently applying a transversely exerted localized compressive force against said surface, and moving over the surface of the substrate substantially rigid shearing means which exerts transversely an applied, localized shear force against the surface and which wipes away exposed portions of silicone polymer composition on the surface, thereby leaving open some of the cells and individually encapsulating at least some of the surface portions of the passageways through the substrate matrix with said silicone polymer composition; and curing the silicone polymer composition in the substrate.

The fluorochemical impregnation operation is conveniently and preferably carried out by the steps of: substantially completely saturating a starting substrate with a solution or dispersion of a fluorochemical composition in a carrier liquid; compressing the saturated substrate to remove therefrom excess portions of said dispersion; and heating said substrate to evaporate the carrier liquid therefrom. However, any convenient process can be used for accomplishing fluorochemical pretreatment of a substrate to be used in this invention.

The following text concerns the theory of the invention as it is now understood; however, there is no intent herein to be bound by theory.

The presently preferred polymer impregnant used in the pressure impregnation and knife blade treatment of substrates by this invention is a non-Newtonian liquid exhibiting thixotropic, pseudo-plastic

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behavior. Such a liquid is temporarily lowered in viscosity by high pressure shear forces.

One aspect of the invention is a recognition that when high forces are applied to curable silicone polymer compositions, such as those as viscous as bathtub caulk, then the viscosities of these materials can be lowered perhaps up to 99% or more. Conversely, when cured (polymerized and/or cross-linked) these compounds increase in viscosity up to perhaps 1,000,000% or more. The internal and external rheological control of viscous silicone impregnant materials achieved by the present invention is believed to be of an extreme level even for thixotropes. When subjected to shear force, the silicone polymer composition can flow more readily, perhaps comparably, to water. When subsequently subjected to curing, the same composition sets to a solid form which can have a consistency comparable to that of a hard elastomeric rubber.

The invention preferably employs a combination of: (i) mechanical pressure to squeeze a silicone polymer composition impregnant into a porous substrate; (ii) porous substrate pretreatment with a water repellent chemical, such as a fluorochemical, which is theorized to reduce the surface tension characteristics of the substrate and create a favorable surface contact angle between the silicone polymer composition and the treated substrate which subsequently allows, under pressure and shear force exerted upon an applied silicone polymer composition, the production and creation of thin enveloping or encapsulating film to form as a result of impregnant flow over the passageways in the matrix of a porous substrate; and (iii) a silicone polymer composition impregnant preferably having favorable rheological and viscosity properties which responds to such working pressures and forces, and

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to be controllably impregnated into, and distributed in a substrate. This combination produces an encapsulated, open cell lined substrate having the capability for a high degree of performance. This product is achieved through pressure impregnation and applied shear forces brought to bear upon a substrate so as to cause controlled movement and flow of a silicone polymer composition into and through a substrate. Preferably, repeated compressive applications of pressure or successive applications of localized shear forces upon the impregnant in the treated substrate are employed.

By the preferred use of such combination, a relationship is established between the respective surface tensions of the impregnant and the substrate, creating a specific contact angle. The impregnant responds to a water repellent fluorochemical pretreatment of the substrate so as to permit enhanced flow characteristics of the impregnant over the substrate and the development of silicone polymer composition encapsulated passageways through the substrate matrix (and lined cell or pore walls) in a treated substrate. However, the boundary or edge of the impregnant is moved, preferably repeatedly, in response to applied suitable forces into the interior region of a porous substrate so as to cause thin films of the impregnant to develop on the interior surfaces of cell or pore walls.

The word "thixotropy" refers herein to liquid flow behavior in which the viscosity of a liquid is reduced by agitation or stirring. It is theorized to be caused by the breakdown of some loosely knit structure in the starting liquid that is built up during a period of rest (storage) and that is torn down during a period of suitable applied stress.

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Thixotropic behavior is preferably built into an impregnant used in the invention. For example, it now appears that thixotropic behavior can be accentuated by introducing into a silicone polymer composition certain additives that are believed to impart enhanced thixotropy to the resulting composition. A lower viscosity at high shear rates (during application to a substrate) is believed to facilitate impregnant flow and application to a substrate, whereas an impregnant with high viscosity, or applied at a low shear rate (before and/or after application) actually may retard or prevent structural element encapsulation and cell wall.

Illustratively, the practice of this invention can be considered to occur in stages:

In stage 1, silicone polymer composition impregnant is prepared which can be purchased commercially and comes in typically two parts, designated as A and B. For example, in a silicone polymer composition as taught in U.S. Patent No. 4,472,470, a base vinyl terminated polysiloxane is the A part, while a liquid organohydrogensiloxane crosslinking agent is the B part. Certain remaining components, such as a resinous organopolysiloxane copolymer and a platinum catalyst may (or can) apparently initially be in either part A or part B.

Stage 2 can be considered to involve the mixing of such a product's parts with or without additives. Changes in viscosity can be obtained and measured based on applied shear rates and shear stresses. Such changes can be experienced by an impregnant with or without additives. Up to a 99% reduction in the viscosity of a liquid silicone polymer composition is believed to be obtainable by the shear forces involved in the mixing or infusion of a silicone polymer composition impregnant into a substrate during,

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the elapsed applied combination of processing time, temperature, radiation, and/or chemical changes involved. Thereafter, a very substantial increase in impregnant viscosity is believed to be obtainable taking
5 into account these same factors. Normally, the most significant factor is now believed to be the mixing shear gradient that typically reduces the viscosity of the impregnant about 50% below the starting or rest viscosity.

10 Stage 3 can be considered to be the pressure introduction stage. Up to a 99% reduction of the impregnant viscosity is believed to be obtainable due to the applied shear forces, elapsed time, temperature, radiation and/or chemical changes. Thereafter, a
15 10,000% increase or even more in the resulting impregnant viscosity is believed to be obtainable. In this stage, curing of the impregnant can take place. Most commonly, impregnant viscosity is decreased during the pressure introduction stage 3 by the application of
20 shear forces.

Stage 4 can be considered to be the first stage internal matrix dispersing and reintroduction with metering, and also recovery and recycle of excess
25 impregnant. Typically, within stage 4, the shear forces cause a temporary lowering of impregnant viscosity, causing it to flow upon and into the three-dimensional structure of the substrate. The initial visco-elastic character of the impregnant is typically theorized to be recovered almost immediately after shear forces are
30 removed.

Stage 5 can be considered to be a second stage internal matrix dispersing and reintroduction with metering and also recovery and recycling of excess
35 impregnant. The variations in the viscosity of the impregnant are equivalent to stage 4. The viscosity of

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the impregnant is again lowered causing it to flow within the substrate. Because of the application of repeated shear force induced reductions in viscosity, the thixotropic behavior of an impregnant may not
5 undergo complete recovery, following each application of shear force and the viscosity of the impregnant may not revert to its pre-impregnation values. The silicone polymer composition impregnant is believed to have the capacity to form a thin film upon the surfaces of
10 components comprising a porous three-dimensional matrix such as a substrate during time intervals that the impregnant is caused to flow under pressure in and about matrix components. In between these times, the impregnant may recover substantially all of its initial
15 high viscosity, although perhaps slightly less so with each repeated application of shearing pressure or force.

Stage 6 can be considered to be occurring just as curing is begun, and just as heat is introduced.

Stage 7 can be considered to be occurring with
20 regard to the exertion of control of curing. Typically, at least a partial curing (including cross-linking and/or polymerizing), is obtained by relatively low temperatures applied for relatively short times, for example, temperatures under about 350°F applied for
25 under about 3 minutes.

Fig. 8, consisting of Figs. 8a through 8d, shows four graphs illustrating four ways that could be used for plotting impregnant rheological behavior: (a) shear rate versus shear stress (uniform scales), (b)
30 shear rate versus shear stress (log scales), (c) viscosity versus shear rate (uniform scales), and (d) viscosity versus shear rate (log scales), if desired, in the practice of this invention. Only the log versus log scales are believed to be capable of encompassing a full
35 range of values for the three indicated variables. The

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graphs represent some broad ranges of viscosity changes relative to shear stress that could be undergone by a given silicone polymer composition impregnant during execution of a given pressured impregnation procedure as taught herein.

For the purposes of the present invention, the term "surface tension" can be considered to refer to a single factor consisting of such variables as intermolecular, or secondary, bonding forces, such as permanent dipole forces, induced forces, dispersion or nonpolar van der Waals forces, and hydrogen bonding forces. The strong primary bonding forces at an interface due to a chemical reaction are theorized to be excluded from surface tension effects; however, it is noted that even a small degree of chemical reactivity can have a tremendous influence on wetting effects and behavior affected by surface tension.

Surface tension is believed to induce wetting effects which can influence the behavior of a silicone polymer composition impregnant relative to the formation of a structural element encapsulation layer therewith in a porous substrate. For example, adhesion is theorized to be a wetting effect. Spontaneous adhesion always occurs for contact angles less than about 90° . However, for a combination of a rough surface and a contact angle over 90° , adhesion may or may not occur. In fact, roughness becomes antagonistic to adhesion, and adhesion becomes less probable as roughness increases.

Also, penetration is theorized to be a wetting effect. Spontaneous penetration occurs for contact angles less than about 90° , and does not occur for contact angles over about 90° . The roughness of a solid surface accentuates either the penetration or the repellency action, but has no influence on which type of wetting takes place.

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In addition, spreading is theorized to be a wetting effect. Retraction occurs for contact angles over 90° or over planar surfaces for any contact angle. However, spontaneous spreading for contact angles less than 90° , especially for small contact angles, may be induced by surface roughness.

Fig. 9 is a schematic vector diagram illustrating the surface tension forces acting at the vertex boundary line of a liquid contact angle on a planar solid surface. It illustrates how surface tension forces might be measured between a silicone polymer composition impregnant and a structural element of a substrate as treated by the invention.

Fig. 10 is a graph relating the contact angle over a smooth solid surface as a function of θ and i that apply respectively, to adhesion ($i \cos \theta$), penetration ($i \cos \theta$), and spreading ($i \cos \theta$).

Regions of adhesion versus adhesion, penetration versus repellency, and spreading versus retraction are shown by shaded areas. Fig. 10 illustrates what is theorized to be the relationship of a silicone polymer composition impregnant to silicone polymer composition solids in a treated substrate as regards such factors as adhesion, penetration, spreading, and retraction.

Fig. 11, consisting of Figs. 11a through 11d, shows representative viscosity profiles plotted on log viscosity versus log shear rate graphs for (a) pseudoplastic flow, (b) distant flow, (c) pseudoplastic flow with superimposed thixotropic behavior, and (d) laminar Newtonian flow that erupts into turbulent flow at a critical transition point.

Figs. 11a through 11d show a broad range of illustrative flow characteristics that could be demonstrated by silicone polymer composition impregnants

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suitable for use in this invention using pressured impregnation of a substrate as taught herein.

For purposes of this invention, the term "wetting" is used to designate such processes as adhesion, penetration, spreading, and cohesion. If wetting transpires as a spontaneous process, then adhesion and penetration are assured when the solid surface tension exceeds the liquid surface tension. Surface roughness promotes these spontaneous wetting actions. On the other hand, no such generalizations can be made when the solid surface tension is less than the liquid surface tension.

Surface tension is measured as by S.T.L. units for liquid and by S.T.S. units for solids; both units are dyns/centimeter. When web S.T.S. is less than S.T.L., then wetting is less ubiquitous and prediction of wetting behavior is more difficult. However, by taking advantage of the liquid/solid contact angle that forms when a liquid retracts over a solid, it is possible to calculate with reasonable accuracy the wetting behavior that can be expected. The reduction in liquid surface area can be computed in terms of the contact angle that the liquid makes with the solid surface. Contact angles are always measured in the liquid phase. There is a point of equilibrium where the surface tension forces become balanced.

By measuring the contact angle of a liquid on a solid, the wetting behavior of the liquid impregnant can be measured.

The following examples are offered to specifically illustrate this invention. These examples are not to be construed as limiting the scope thereof, however.

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Example 1: Liquid Silicone Polymer Preparation

100 parts by weight of the curable liquid
silicone polymer available commercially from Mobay as
"Silopren® LSR 2530" was mixed in a 1:1 ratio, as
5 recommended by the manufacturer. A Hockmayer F
dispersion blade at low torque and high shear was used
to do the mixing. To this mixture were added 5 parts by
weight of BSF "Uvinul 400" and 5/10 parts by weight Dow
Corning 7127 accelerator, believed to be a polysiloxane
10 but containing an undisclosed active accelerated
ingredient.

Examples 2-19: Liquid Silicone Polymer Preparation

The procedure of Example 1 was repeated with
various other curable viscous liquid silicone polymer
15 composition commercially available. To this product
system is added a substituted benzophenone and other
additives, the result of which are shown in Table VI
below. All parts are by weight.

20

Table VI
Illustrative Silicone Resin Compositions

Example #	Starting Silicone Resin	Mixture Ratio of Packaged Components	Substituted Benzophenone Name	Parts	Other Additives Name	Parts
1	Silopren® LSR 2530	1:1	Uvinul 400	5	7127 Accelerator	5/10
2	Silastic® 595 LSR	1:1	Uvinul 400	5	Syl-off® 7611 ⁽²⁾	50
3	SLE 5100 Liquid BC-10	10:1 1:1 1:1	Uvinul 400	5	Sylox® 2 ⁽³⁾	8
4	Silopren® LSR 2530	1:1	Uvinul 400	5	Hydral® 710 ⁽⁴⁾	10
5	Silopren® LSR 2530	1:1	Uvinul 400	5	Silopren® LSR Z3042 ⁽⁵⁾	1
6	SLE 5500	10:1	Uvinul 400	5		
7	Silopren® LSR 2540	1:1	Uvinul 400	5		
8	SLE 5300	10:1	Uvinul 400	5		
9	SLE 5106	10:1	Uvinul 400	5		
10	Silopren® LSR 2530	1:1	Uvinul 400	5	Flattening Agent OK412® ⁽⁶⁾	4
11	Silopren® LSR 2530	1:1	Uvinul 400	5	Nalco ⁽⁵⁾ 1SJ-612 Colloidal Silica ⁽⁷⁾	50
12	Silopren® LSR 2530	1:1	Uvinul 400	5	Nalco® 1SJ-614 Colloidal Alumina ⁽⁸⁾	
13	Silastic® 595 LSR	1:1	Uvinul 400	5	200 Fluid ⁽⁷⁾	7

Table VI (Cont.)
Illustrative Silicone Resin Compositions

Example #	Starting Silicone Resin	Mixture Ratio of Packed Components ¹	Substituted Benzophenone		Other Additives	Parts
			Name	Parts	Name	
14	Silopren® LSR 2530	1:1	Uvinul 400	5		
15	Silastic® 595 LSR	1:1	Uvinul 400	5	Zepel® 7040 ⁽¹⁰⁾	3
16	Silastic® 595 LSR	1:1	Uvinul 400	5	Zonyl® UR ⁽¹¹⁾	1/10
17	Silastic® 595 LSR	1:1	Uvinul 400	5	Zonyl® FSN-100 ⁽¹²⁾	1/10
18	Silopren® LSR 2530	1:1	Uvinul 400	5	DLX-600® ⁽¹³⁾	5
19	Silopren® LSR 2530	1:1	Uvinul 400	5	TE-3608® ⁽¹⁴⁾	5

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Table VI Footnotes:

- 5 (1) Ratio listed is that recommended by the manufacturer.
- (2) Syl-off® (registered trademark of Dow Corning) is a cross-linker.
- 10 (3) Sylox® 2 (registered trademark of W.R. Grace & Co.) is a synthetic amorphous silica.
- (4) Hydral® 710 (registered trademark of Alcoa) is a hydrated aluminum oxide.
- 15 (5) Silopren® LSR Z/3042 (registered trademark of Mobay) is a silicone primer (bonding agent) mixture.
- 20 (6) Flattening Agent OK412® (registered trademark of Degussa Corp.) is a wax coated silicon dioxide.
- (7) Nalco® 1SJ-612 Colloidal Silica (registered trademark of Nalco Chemical Company) is an aqueous solution of silica and alumina.
- 25 (8) Nalco® 1SJ-614 Colloidal Alumina (registered trademark of Nalco Chemical Company) is an aqueous colloidal alumina dispersion.
- 30 (9) 200 Fluid (registered trademark of Dow Corning) is a trimethyl silyl endblocked polydimethylpolysiloxane.
- 35 (10) Zepel® 7040 (registered trademark of duPont) is a nonionic fluoropolymer.
- (11) Zonyl® UR (registered trademark of duPont) is an anionic fluorosurfactant.
- 40 (12) Zonyl® FSN-100 (registered trademark of duPont) is a nonionic fluorosurfactant.
- (13) DLX-6000® (registered trademark of duPont) is a polytetrafluoroethylene micropowder.
- 45 (14) TE-3608® (registered trademark of duPont) is a polytetrafluoroethylene micropowder.
- 50

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Example 20: Impregnation of an Open Cell Material

A complete, stepwise, application of the inventive method in the production of an encapsulated-material was as follows.

5 The selected base material was Mobay Bayer tan leather #80118 supplied for Adidas.

 The material was weighed and measured. Its initial weight is 19.7 ounces per square yard. Its thickness equals 52 mils.

10 The material was soaked in water, wrung dry, and weighed. The water retained was equal to 1.13 g water/g fabric.

 The material was next washed with a detergent, rinsed thoroughly, and hung to air dry.

15 The material was then treated with a water repellant fluorochemical, a 3% solution by weight of Milease® F-31X. In order to do so the fabric was soaked in a 2.7% solution of Milease® water repellant chemical in distilled water. This was because

20 $\frac{1 \text{ g fabric } (.03)}{1.13 \text{ g water}} = 0.027$

 The treated material was then run through a wringer and air dried.

25 Next, the material was heated in an oven for 3 minutes at 350°F. This heating sinters the water repellant fluorochemical.

30 Next the material with its fluorochemical residue was pulled through opposed blades with a gap of 40 mils of an impregnation apparatus as shown in Fig. 4a at ambient conditions. The silicone impregnation material (a 1:1 mixture of Mobay LSR 2530 A/B and 5% Uvinul) was spread on the material with a spatula prior to pulling it through the apparatus. The impregnant was put on the smooth side. The impregnant can be
35 considered to be a visco-elastic liquid that flows only

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under the shear forces resulting from the pressured impregnation. The impregnant is believed to substantially return to its original viscous condition almost immediately upon release of the pressure. The impregnant was believed to flow a short distance within the open cell construction leather during the short time that it was, because of pressure shearing forces, of lowered viscosity.

The impregnated material was cured in an oven for 5 minutes at 350°F. A top coat of General Electric SLC 5106 A/B mixed in a 10:1 ratio was then applied to the cured impregnated sample. The sample was pulled through the blades at a gap width of 45 mils. Finally, the material was cured for 5 minutes at 350°F. The resultant material has a non-tacky thin film of silicone impregnating an open cell material keeping the cells substantially open.

Example 21: Impregnation of an Open Cell Material

The test results of the original versus the produced material of Example 20 were as follows:

Table VII

	Original Fabric <u>Smooth/Rough</u>	Impregnated Only <u>Smooth/Rough</u>	Impregnated w/Top Coat <u>Smooth/Rough</u>
Spray Rating (1)	0/0	60/60	80/90
Rain Test (2)	fail/ -	pass/ -	pass/ -
MVTR (g/m ² /day) (3)	636	579	-
Amount Impregnated (oz/yd ²)	-	2.3	3.3
QUV Rating (42 hours)	3	6	-

Footnotes on Table VII:

(1) The spray test was conducted in accordance with AATCC 22-1974. It measures water

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repellency of a fabric sample on a scale of 0-100 with a reading of 100 designating a completely water repellent fabric.

(2) The rain test was conducted in accordance with AATCC 35-1985. It measures resistance of a fabric sample to penetration of water under static pressure from a shower head of 3 feet/5 minutes. A fabric is stormproof when less than 1.0 gram of water is absorbed by a standardized blotter used in the test.

(3) The moisture vapor transmission (MVTR) test was conducted in accordance with ASTM E96-B. The test measures the amount of moisture vapor passing through a fabric sample in a controlled environment during a 24 hour period. The obtained MVTR figure is expressed in grams of water/square meter of surface/24 hour day. The environmental chamber was held at 104°F and 47% humidity.

Example 22: Impregnation of an Open Cell Material

A complete, stepwise, application of the inventive method in the production of an impregnated open cell material, namely leather was as follows.

The selected base material was Adidas White Texas Leather #80226.

The leather was weighed and measured. Its initial weight is 37.4 ounces per square yard. Its thickness equals 54.74 mils.

The leather was soaked in water, wrung dry, and weighed. The water retained was equal to 0.209g/g material.

The leather was next washed with a detergent, rinsed thoroughly, and hung to air dry.

The leather was then treated with a water repellant fluorochemical, a 3% solution by weight of Milease® F-31X. In order to do so the fabric was soaked

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in a 15% solution of Milease® water repellent chemical in distilled water. This was because

$$\frac{1 \text{ g leather } (.03)}{0.20 \text{ g water}} = 0.15$$

5 The treated leather was then run through a wringer and air dried.

Next, the leather was heated in an oven for 2 1/2 minutes at 320°F. This heating sinters the water repellent fluorochemical.

10 Next the leather with its fluorochemical residue was pulled once through opposed blades with a gap of 47 mils of an impregnation apparatus as shown in Fig. 4a at ambient conditions. The silicone
15 impregnation material (a 1:1 mixture of Mobay LSR 2530 A/B) was spread on the fabric with a spatula prior to pulling it through the apparatus. The impregnant was put on the smooth side. A top coat of General Electric SLC 5106 A/B, mixed in a 10:1 ratio, was subsequently applied and pulled through opposed blades in the same
20 manner as the Mobay 2530 A/B. The impregnant can be considered to be a visco-elastic liquid that flows only under the shear forces resulting from the pressured impregnation. The impregnant is believed to return very substantially to its original viscous condition almost
25 immediately upon the release of the pressure. The impregnant was believed to flow a short distance within the open cell construction of the leather during the short time that it was, because of pressure shearing forces, of lowered viscosity. Therefore, a number of
30 "flows" may be usefully generated in order to properly distribute the impregnant in its preferred position substantially impregnating the open cells of the leather while keeping the cells substantially open.

35 Finally, the impregnated leather was cured in an oven for 2 1/2 minutes at 320°F. The resultant

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leather has a non-tacky thin film of silicone substantially impregnating the open cells on the surface of the leather while keeping the cells open.

Example 23: Impregnation of an Open Cell Material

5 The tests results of the original versus the produced impregnated open cell material of Example 24 were as follows:

<u>Leather</u>	<u>Original Smooth/Rough</u>	<u>Impregnated Smooth/Rough</u>
10 Spray Rating	90/50	100/90
Rain Test	Pass/Pass	Pass/Pass
15 Weight (oz/yd ²)	37.4	40.4

Silicone Add-on = 3.0 oz/yd²

Accelerated Weathering Test

20 Samples placed in QUV weatherometer for 104 hours

Original = 3

25 Impregnated side = 6

Example 24: Impregnation of an Open Cell Material

30 A complete, stepwise, application of the inventive method in the production of an encapsulated-fiber fabric was as follows.

The selected base material was Brown Leather #80118 supplied by Mobay Bayer.

35 The material was weighed and measured. Its initial weight is 19 ounces per square yard and its thickness is 45 mils.

The material was next washed with a detergent, rinsed thoroughly, and hung to air dry.

40 The material was then treated with a water repellent fluorochemical, a 3% solution by weight of Milease® F-31X.

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The treated material was then run through a wringer and air dried.

Next, the material was heated in an oven for 3 minutes at 350°F. This heating sinters the water repellant fluorochemical.

Next the material with its fluorochemical residue was pulled through opposed blades with a gap of 32 mils of an impregnation apparatus as shown in Fig. 4a at room ambient conditions. The silicone impregnation material (a mixture of Mobay 2530 A/B with a 5% Uninul 400) was spread on the material with a spatula prior to pulling it through the apparatus. The impregnant was put on the smooth side. The impregnant can be considered to be a visco-elastic liquid that flows only under the shear forces resulting from the pressured impregnation. The impregnant is believed to return very substantially to its original viscous condition almost immediately upon release of the pressure. The impregnant was believed to flow a short distance within the open cells of the material during the short time that it was, because of pressure shearing forces, of lowered viscosity.

The impregnated material was cured in an oven for 5 minutes at 350°F. A top coat consisting of General Electric SLC 5106 A/B (mixed in a 10:1 ratio) was then applied to the material. The sample was pulled through the blades at a gap width of 45 mils. The material was then cured for 5 minutes at 350°F. The resultant material has a non-tacky thin film of silicone substantially impregnating the open cells of the leather leaving the cells substantially open.

Example 25: Impregnation of Open Cell Material

The test results of the original versus the produced fiber encapsulated fabric of Example 26 were as follows:

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5	<u>Material</u>	<u>Original Smooth/Rough</u>	<u>Encapsulated Smooth/Rough</u>	<u>Top Coat Smooth/Rough</u>
	Spray Rating	0/0	80/80	90/80
	Rain Test	Fail	Pass	Pass
10	Weight	19 oz/yd ²	-	21.7 oz/yd ²
	QUV (16 hrs)	6	6	-

15 Accelerated Weathering Test

Samples placed in QUV weatherometer for 16 hours.

20 Original = 6

Impregnated side = 6

(readings based on color scale of 0 = 10, 10 = original color, 0 = white out)

25 Example 26: Impregnation of an Open Cell Material

A complete, stepwise, application of the inventive method in the production of an encapsulated material was as follows.

30 The selected base material was 9-70-3 Blue Leather #80118 supplied by Mobay Bayer for Adidas.

The material was weighed and measured. Its average initial weight is 22.8 ounces per square yard and its thickness is 47 mils.

35 The material was washed with a detergent, rinsed thoroughly, and hung to air dry.

The material was then treated with a water repellent fluorochemical, a 3% solution by weight of Milease® F-31X.

40 The treated material was then run through a wringer and air dried.

Next, the material was heated in an oven for 3 minutes at 350°F. This heating sinters the water

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repellant fluorochemical.

Next the material with its fluorochemical residue was pulled through opposed blades with a blade gap of 47 mils of an impregnation apparatus as shown in Fig. 4a at room ambient conditions. The silicone impregnation material (a 1:1 mixture of Mobay 2530 A+B with a 5% Uninul 400) was spread on the material with a spatula prior to pulling it through the apparatus. The impregnant was put on one only, upper, smooth side. The impregnant can be considered to be a visco-elastic liquid that flows only under the shear forces resulting from the pressured impregnation. The impregnant is believed to return very substantially to its original viscous condition almost immediately upon release of the pressure. The impregnant was believed to flow a short distance within the open cell construction leather during the short time that it was, because of pressure shearing forces, of lowered viscosity.

Finally, the impregnated material was cured in an oven for 5 minutes at 350°F. The resultant material has a non-tacky thin film that substantially impregnates the open cell material keeping the cells substantially open.

Example 27: Impregnation of an Open Cell Material

The test results of the original versus the produced fiber encapsulated material of Example 22 were as follows:

<u>Fabric</u>	<u>Original Smooth/Rough</u>	<u>Leather Impregnant Only Smooth/Rough</u>	<u>Impregnant w/Top Coat Smooth/Rough</u>
Spray Rating	0/0	100/100	100/100
Rain Test	Fail	Pass	Pass
Weight (oz/yd ²)	22.8	-	26.8

Amount Impregnated = 4 oz/yd²

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The spray test was conducted in accordance with AATCC 22-1974. It measures water repellency on a scale of 0-100, with a reading of 100 being completely water repellent.

Example 28: Fiber Encapsulated Fabric Preparation

A complete, stepwise, application of the inventive method in the production of an encapsulated-fiber fabric was as follows.

The selected base material was 100% white chloroprene rubber #80123 available from Rip Curl covered with green and purple 100% polyester knit fabric.

The fabric was weighed and measured. Its initial weight is 23.7 ounces per square yard. Its thickness equals 93 mils.

The fabric was soaked in water, wrung dry, and weighed. The water retained was equal to 0.27 g water/g fabric.

The fabric was then treated with a water repellant fluorochemical, a 3% solution by weight of Milease® F-31X. In order to do so the fabric was soaked with an 11% solution of Milease® water-repellant chemical in distilled water. This was because

$$\frac{1 \text{ g fabric } (.02)}{0.27 \text{ g water}} = 0.11$$

The treated fabric was then run through a wringer and air dried.

Next, the fabric was heated in an oven for 3 minutes at 350°F. This heating sinters the water repellant fluorochemical.

Next the material with its fluorochemical residue was pulled through opposed blades with a gap width of 47 mils of an impregnation apparatus as shown in Fig. 4a at ambient conditions. The silicone

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impregnation material (a 10:1 mixture of General Electric SLC 5106 A/B with 5% Uninul 400) was spread on the green side of the fabric with a brush or towel prior to pulling it through the apparatus. Normally, the impregnant was put on only one, upper, side. Multiple process stages of pulling the fabric with applied impregnant through the blades are preferably made. The multiple process stages are important, and are normally necessary. The impregnant can be considered to be a visco-elastic liquid that flows only under the shear forces resulting from the pressured impregnation. The impregnant is believed to flow a short distance within the matrix of the fabric during the short time that it was, because of pressure shearing forces, of lowered viscosity. Therefore, a number of "flows" may be usefully generated in a number of passes in order to properly distribute the impregnant in its preferred position substantially encapsulating the surfaces of the fabric's fibers.

Finally, the impregnated fabric was cured in an oven for 5 minutes at 350°F. The resultant fabric has a non-tacky thin film of silicone substantially encapsulating substantial part of the fabric's fibers.

Example 29: Evaluation of Fiber Encapsulated Fabric

Properties

The test results of the original versus the produced fiber encapsulated fabric of Example 28 were as follows:

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<u>Fabric</u>	<u>Original Fabric</u>	<u>Encapsulated</u>
Spray Rating	70	90
Spray Absorption	21%	6%
Rain Test	Pass	Pass
5 Immersion Absorption	18%	12%
Abrasion Test (cycles)	2,600	5,700
QUV Rating (158 hrs)	5	6
Weight (oz/yd ²)	23.7	25.8

Amount Impregnated = 2.1 oz/yd²

10 The spray test was conducted in accordance with AATCC 22-1974. It measures water repellency on a scale of 0-100, with a reading of 100 being completely water repellent.

15 The spray absorption test was conducted in accordance with Federal Test Method Standard #191A.

It is the same method as spray test, except distance from the center of the nozzle to the center of the test sample is 24 inches (instead of 6 inches), and 500 ml. of water is used (instead of 250 ml.). The sample is weighed before and after, and the spray absorption determined:

$$\text{Percent} = \frac{W - O}{O} \times 100$$

W = wet weight, O = dry weight

25 The immersion absorption test was conducted in accordance with Federal Test Method Standard #191A. In this test, a sample approximately 6 inches by 6 inches is weighed, is dropped into a bucket with sufficient water to cover the entire sample. After 20 minutes, the sample is removed from the clamp, run once through the wringer, and weighed. The immersion absorption is determined:

$$\text{Percent} = \frac{F - O}{O} \times 100$$

35 F = final weight, O = original weight

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Example 30: Description of an Impregnated Open Cell
Material Trough Scanning Electron Photomicrographs

Figures 2, 3a and 3b were taken using a Cambridge 360 scanning electron microscope. The samples were cut using teflon coated razor blades, mounted on 1/2 inch diameter aluminum stubs, and coated with a gold/palladium allow.

The sample prior to the treatment of the present invention is shown in Figure 2. The open cells appear quite deep as indicated by the dark shadows.

Figure 3a shows the leather silicone application. The surface of the leather has a thin film of the silicone on it, as seen by the "softening" of the edges of the open cells. The open cells do not appear as deep as before, yet they are left substantially open after application of the silicone impregnant.

The cross-section of the treated sample (Figure 3b) shows a very thin film of silicone along the upper edge. In the photomicrograph, this thin film appears as a continuous gray line following the surface contours. Using the 500 um scale in the legend of the photomicrograph, the thickness of the silicone layer is estimated to be approximately 20 um.

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What is claimed is:

1. A flexible, porous substrate having a matrix with open cells therein, at least some of said cells being at least partially individually lined with a silicone polymer composition, and at least some of said cells being open.
2. The substrate of Claim 1 wherein said silicone polymer composition has an uncured liquid viscosity of at least about 1,000 and no more than about 2,000,000 centipoise.
3. The substrate of Claim 1 wherein said silicone polymer is cured and elastomeric.
4. The substrate of Claim 1 wherein said substrate is a leather.
5. The substrate of Claim 1 wherein said substrate is a porous paper.
6. The substrate of Claim 1 wherein said substrate is an open celled foamed plastic structure.
7. The substrate of Claim 1 wherein said substrate is a synthetic leather.
8. The substrate of Claim 1 wherein said substrate comprises a laminate comprising a layer of an open celled porous flexible material and a layer of a non-porous, flexible material.
9. The substrate of Claim 1 wherein the quantity of said silicone polymer composition is in the range of about 5 to about 200 weight percent of the weight of untreated substrate.
10. The substrate of Claim 9 wherein said substrate is water resistant and rewashable.
11. The substrate of Claim 1 which has been impregnated with a fluorochemical prior to treatment with the silicone polymer.
12. The substrate of Claim 11 wherein the quantity of said fluorochemical is in the range of about

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0.01 to about 5 weight percent of the weight of untreated substrate.

13. The substrate of Claim 12 wherein said silicone polymer composition is cured and wherein the total weight of said fluorochemical and said silicone polymer composition is in the range of about 5 to about 200 weight percent of the total weight of untreated substrate.

14. The substrate of claim 13 wherein said silicone polymer composition contains a benzophenone.

15. A fluorochemical and silicone resin treated porous substrate which is breathable, water resistant and rewashable comprising:

(A) a tensionable porous substrate having opposed, substantially parallel surfaces and comprised of a matrix having open cells therein;

(B) said substrate having been preliminarily generally uniformly impregnated with a fluorochemical; and

(C) said substrate having been thereafter impregnated with a silicone polymer composition that is present in amount in the range from about 5 to about 200 weight percent of the weight of the untreated substrate.

16. The substrate of claim 15 wherein said substrate is also laterally tensionable.

17. The substrate of claim 15 wherein said substrate is a leather.

18. The substrate of claim 15 wherein said substrate is a porous paper.

19. The substrate of claim 15 wherein said substrate is an open-celled plastic structure.

20. The substrate of claim 15 wherein said substrate is a synthetic leather.

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21. The substrate of claim 15 wherein said substrate comprises a layer of an open celled, porous, flexible material and a layer of a non-porous flexible material.

5 22. The substrate of Claim 15 which is characterized by having:

(A) a water drop contact angle in the range of about 90° to about 160°;

10 (B) a rewash capability of at least about 3;

(C) a breathability of at least about 35% of untreated substrate fabric; and

(D) a water repellency rating of at least about 80 prior to washing.

15 23. A process for making the porous substrate of Claim 1 comprising the steps of:

(A) applying a curable silicone polymer composition having a viscosity sufficient to line the walls of said cells to at least one surface and then

20 (B) moving over and against said surface of the resulting substrate with said substrate so tensioned at least one of a uniformly applied compressive force and a uniformly applied localized shear force to

25 - distribute said composition within said substrate generally uniformly,

- at least partially individually line cell walls of at least some of said cells with said composition, and

30 - leave most of said cells open.

24. The process of Claim 23 wherein said polymer composition has a viscosity greater than about 5,000 and less than about 2,000,000 centipoise.

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25. The process of Claim 24 wherein the substrate is subjected to conditions sufficient to cure the silicone polymer composition in said substrate.

5 26. The process of Claim 25 wherein said curing is accomplished by heat.

27. The process of Claim 25 wherein said curing is accomplished by radiation.

10 28. A process for making a fluorochemical and silicone resin treated substrate having breathability, water resistance and rewashability comprising the successive steps of:

(A) impregnating a porous substrate having generally open cells therein, with a fluorochemical;

15 (B) applying a curable silicone polymer composition and concurrently applying a transversely exerted localized compressive force against one surface of the substrate;

20 (C) moving over said surface of the substrate a substantially rigid shearing means which exerts transversely applied localized shear force against said surface and which wipes away exposed portions of silicone polymer composition on said surface, thereby forming an internal layer of silicone
25 polymer composition; and

(D) curing the silicone polymer composition in said substrate.

30 29. The process of Claim 28 wherein said fluorochemical impregnated substrate is both longitudinally and laterally tensioned.

30 30. The process of Claim 28 wherein said porous substrate is a leather.

31. The process of Claim 28 wherein said porous substrate is a porous paper.

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32. The process of Claim 28 wherein said porous substrate is an open-celled plastic.

33. The process of Claim 28 wherein said porous substrate is an open-celled sheet structure.

5 34. The process of Claim 28 wherein said substrate is a synthetic leather.

35. The process of Claim 28 wherein said substrate comprises a layer of a open celled, porous, flexible material and a layer of a non-porous flexible material.

10

36. The process of Claim 28 wherein said fluorochemical impregnating is carried out by the steps comprising:

(A) substantially completely saturating said substrate with a dispersion of a fluorochemical containing composition in a carrier liquid;

15

(B) compressing the saturated substrate to remove therefrom excess portions of said dispersion; and

20 (C) heating said substrate to evaporate said carrier liquid therefrom.

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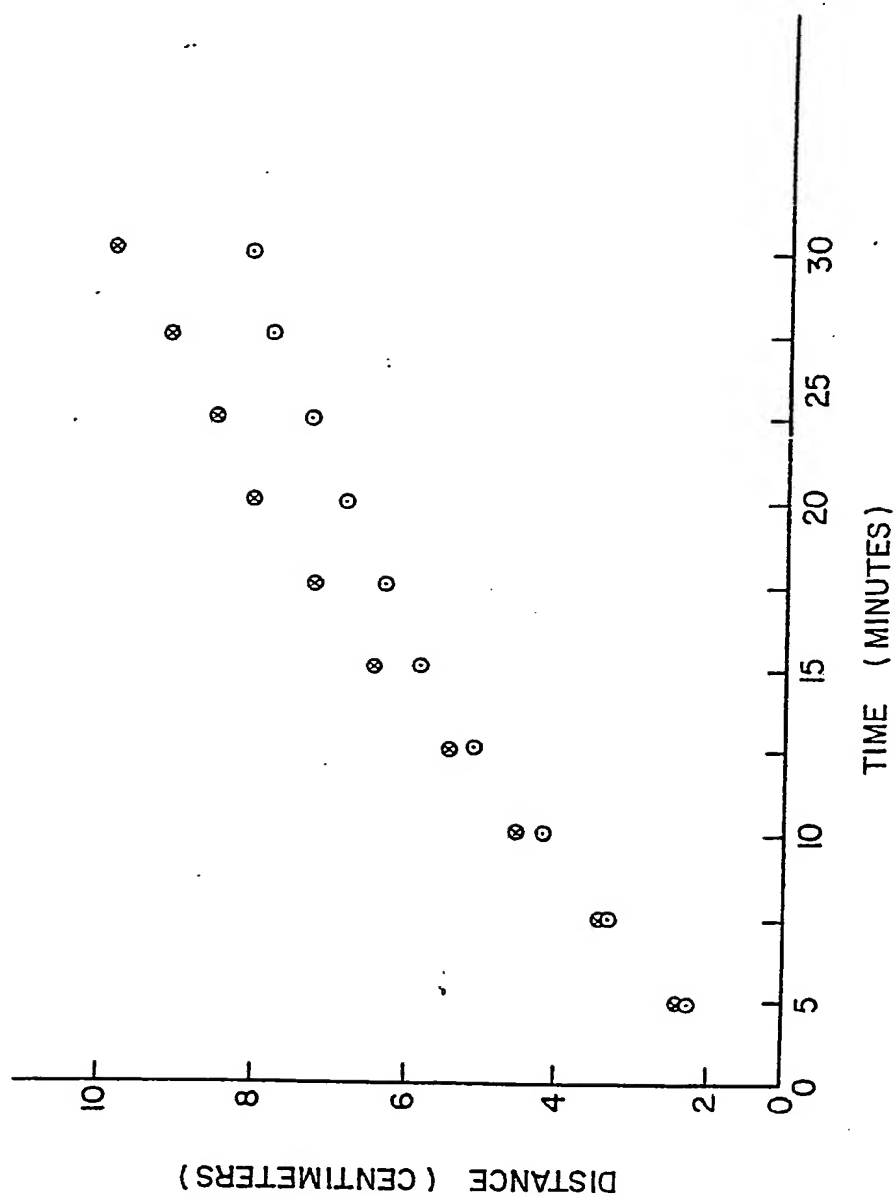


FIG. 1

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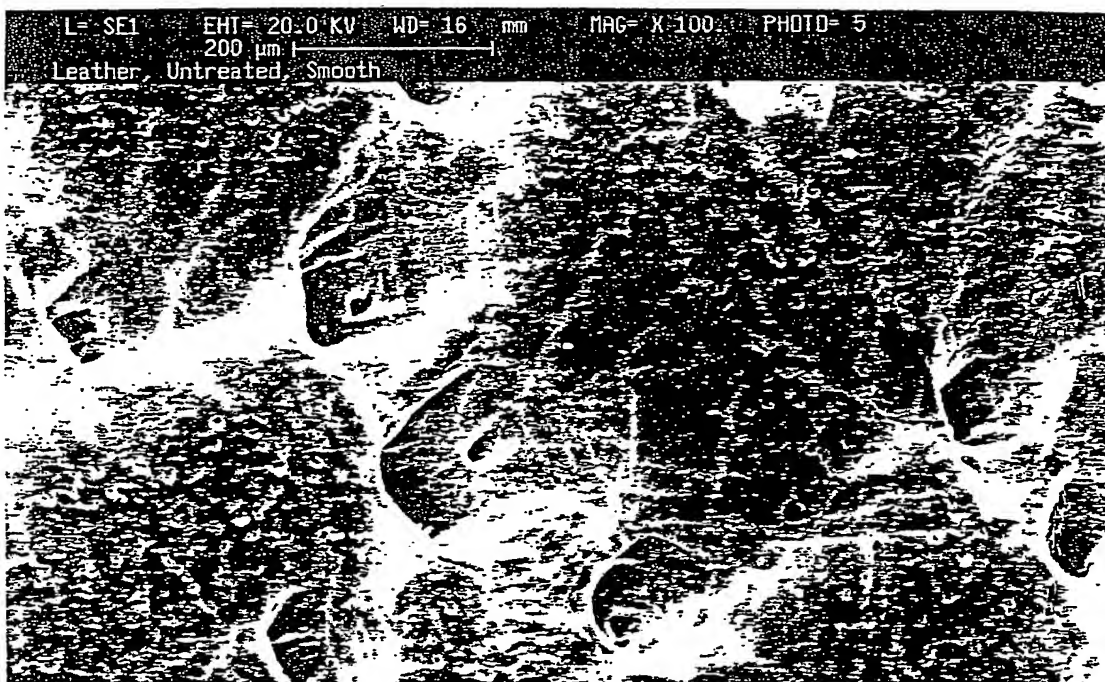


FIG. 2

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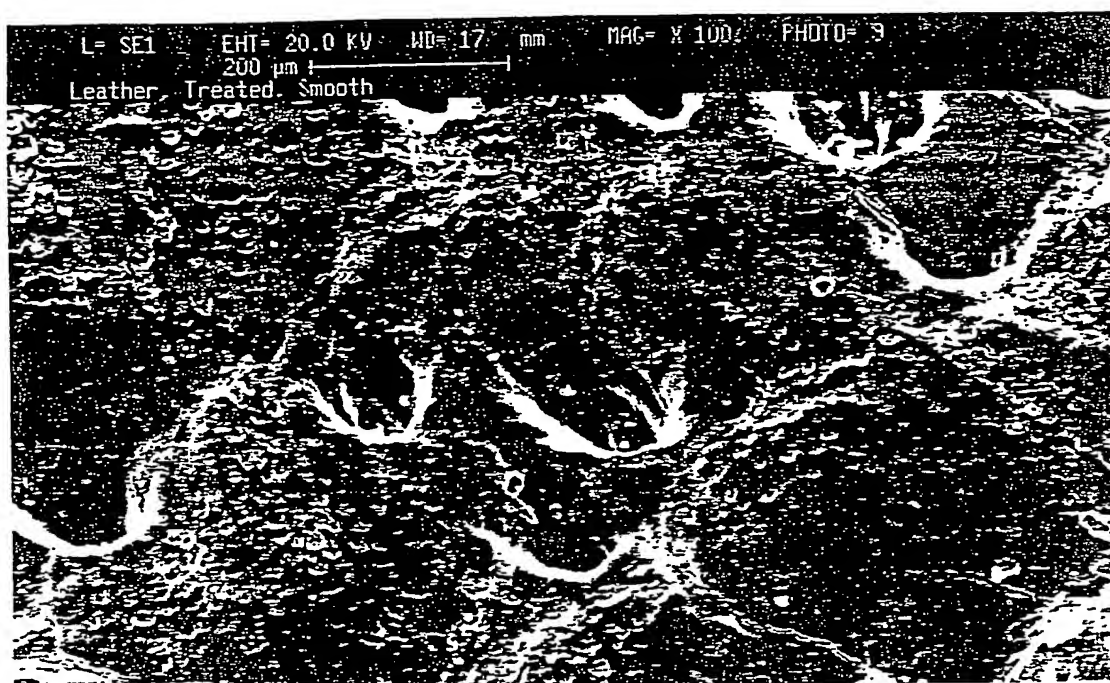


FIG. 3a

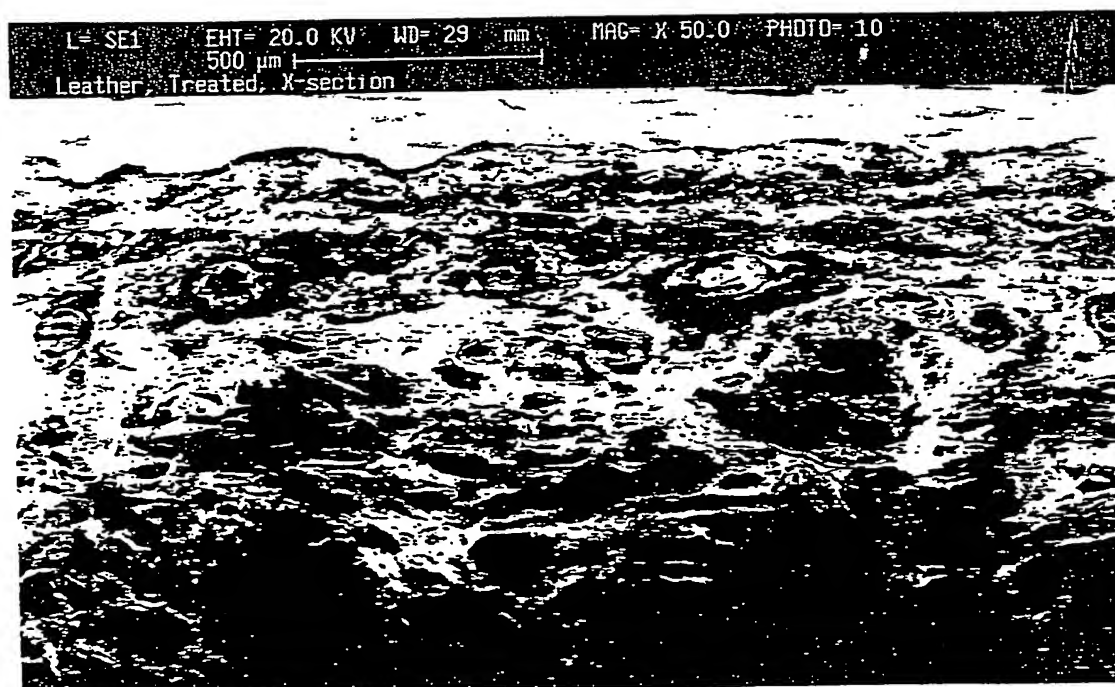


FIG. 3b

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FIG. 4a

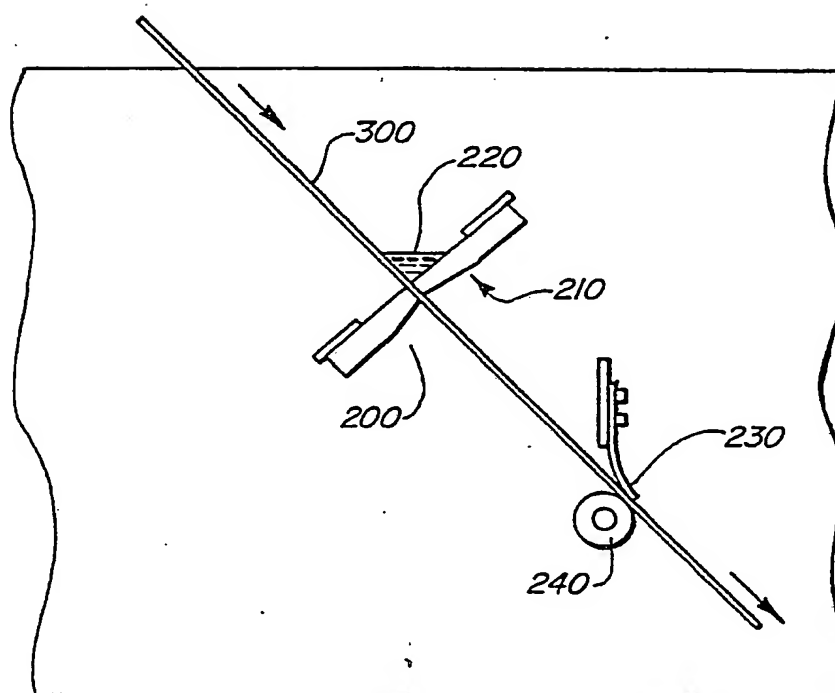
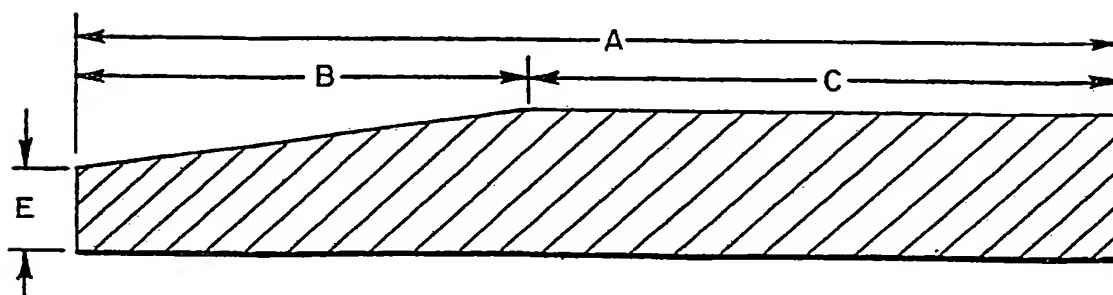


FIG. 4b



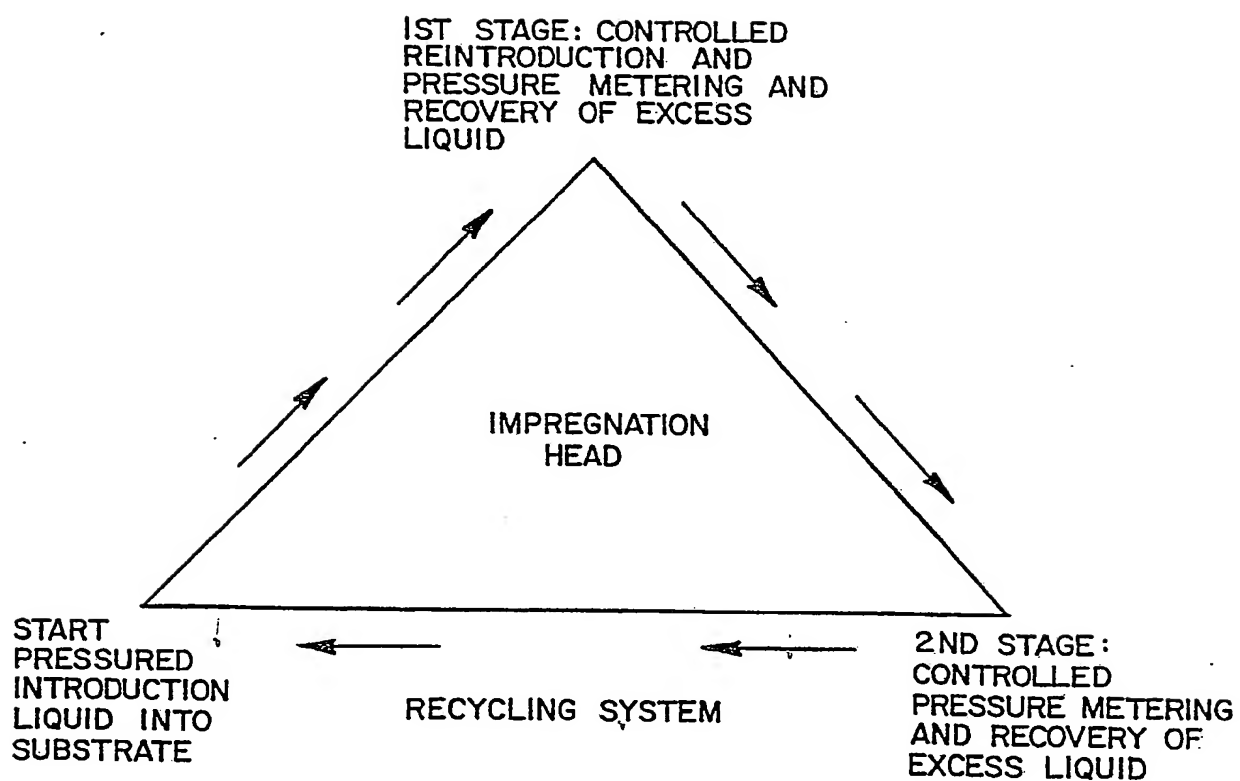
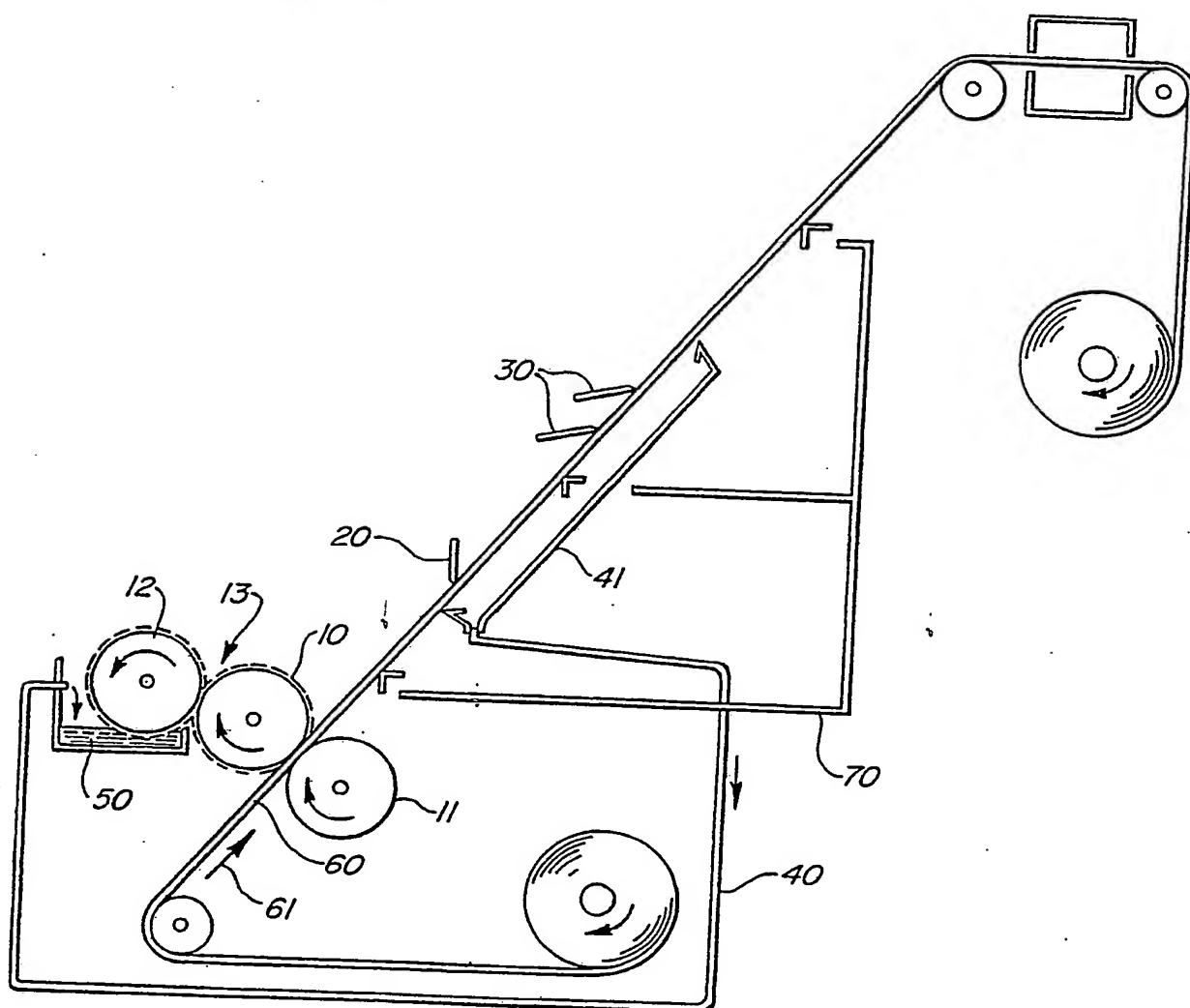


FIG. 5

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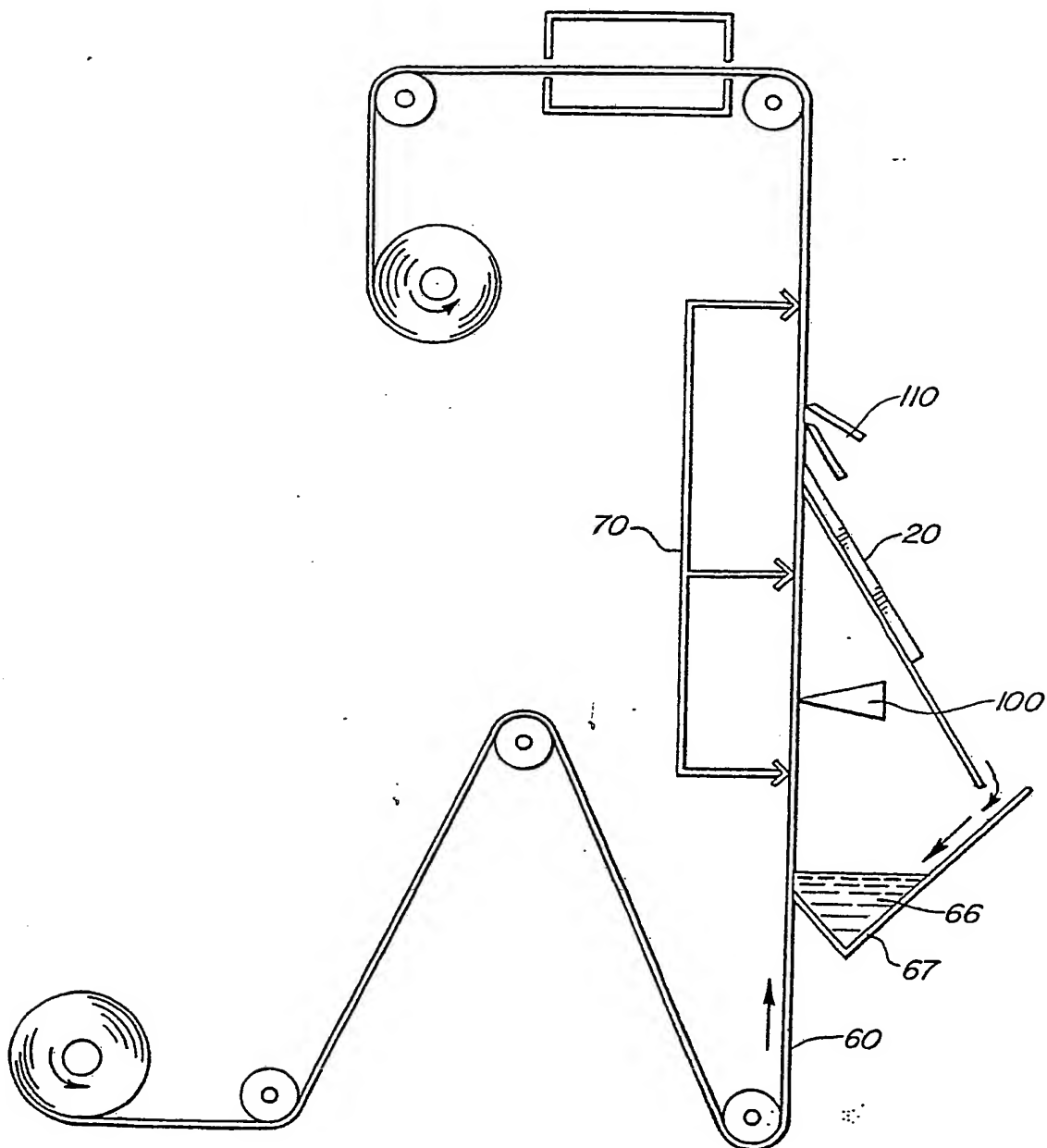
FIG. 6



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FIG. 7



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FIG. 8a PRIOR ART

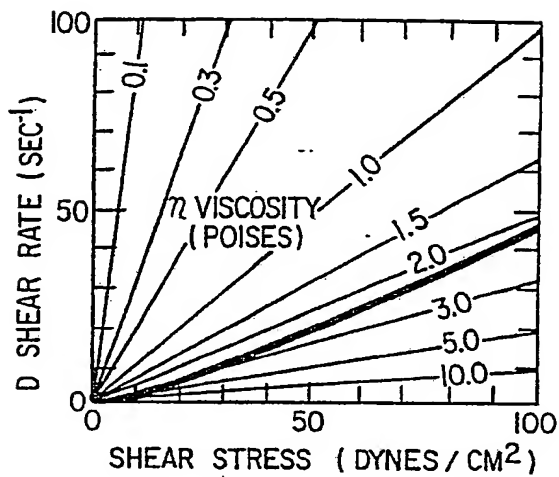


FIG. 8b PRIOR ART

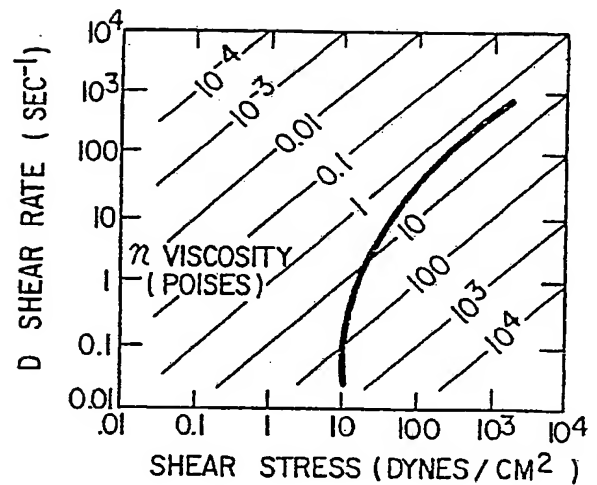


FIG. 8c PRIOR ART

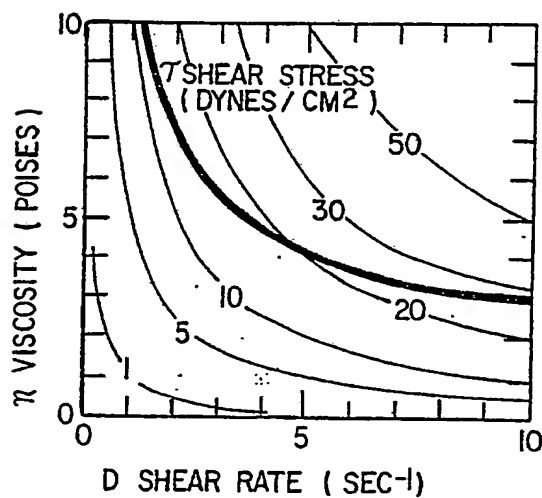
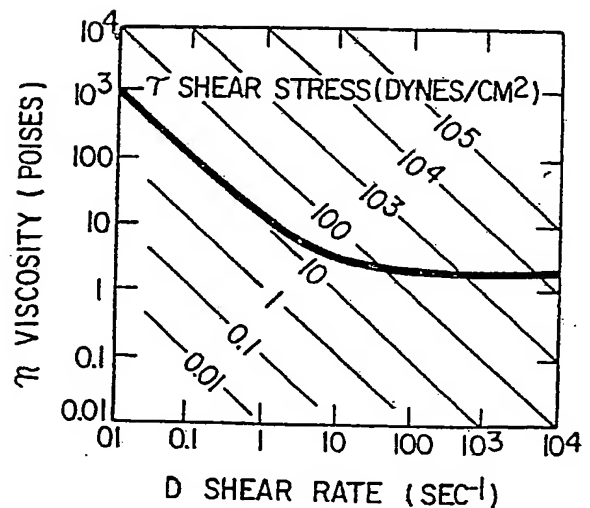


FIG. 8d PRIOR ART



SUBSTITUTE SHEET

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FIG. 9 PRIOR ART

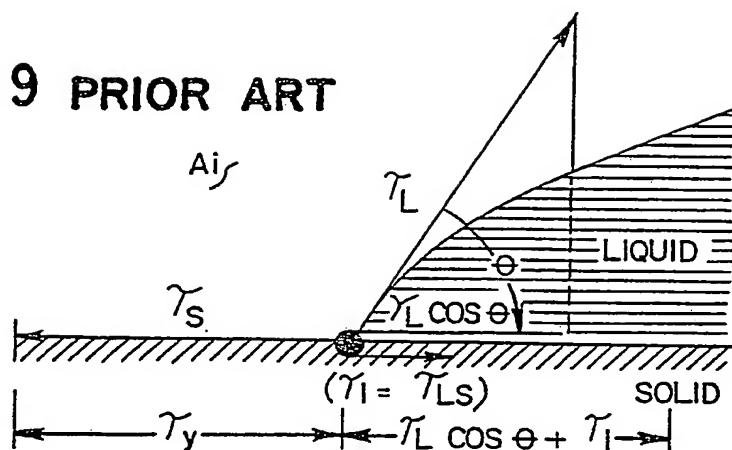
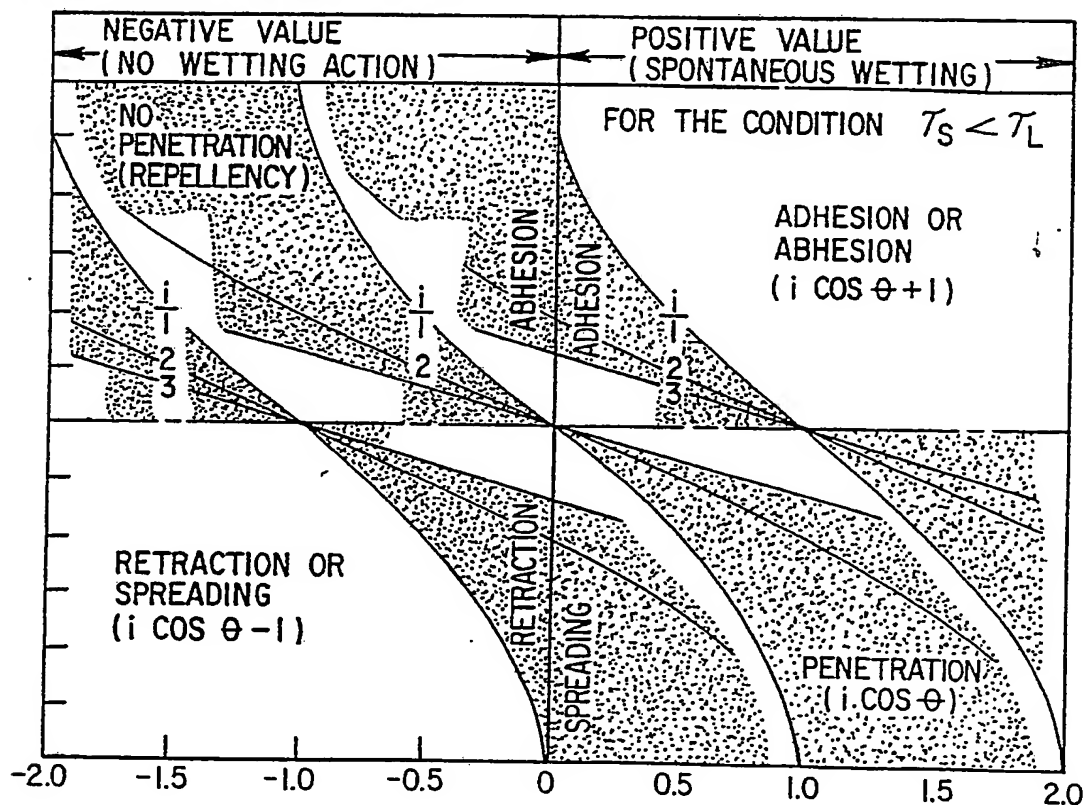


FIG. 10 PRIOR ART



FUNCTION OF θ AND i AS INDICATED ON DIAGRAM FOR ADHESION, PENETRATION, AND SPREADING, RESPECTIVELY

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FIG. 11a PRIOR ART

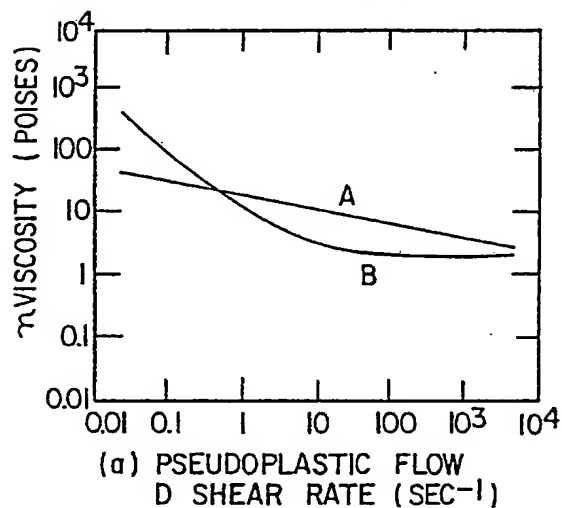


FIG. 11b PRIOR ART

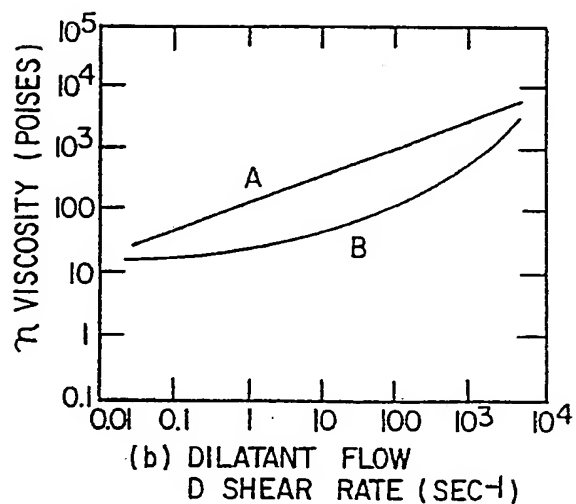


FIG. 11c PRIOR ART

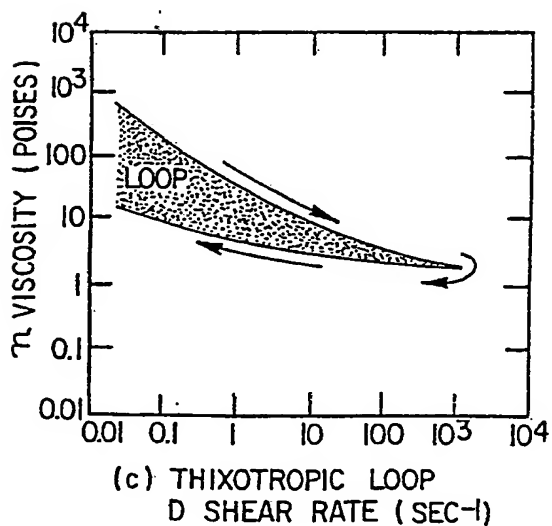
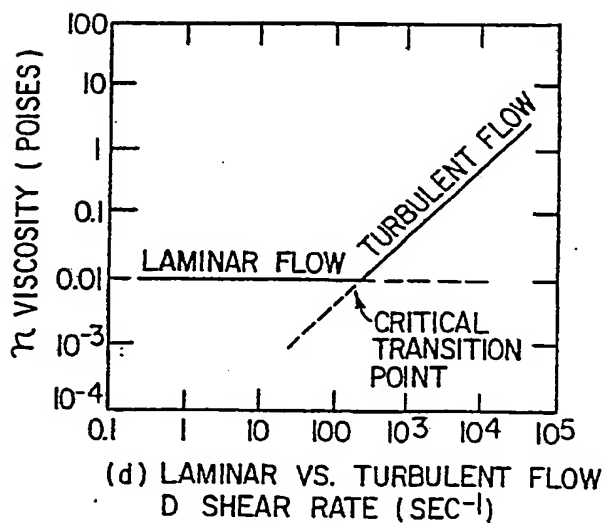
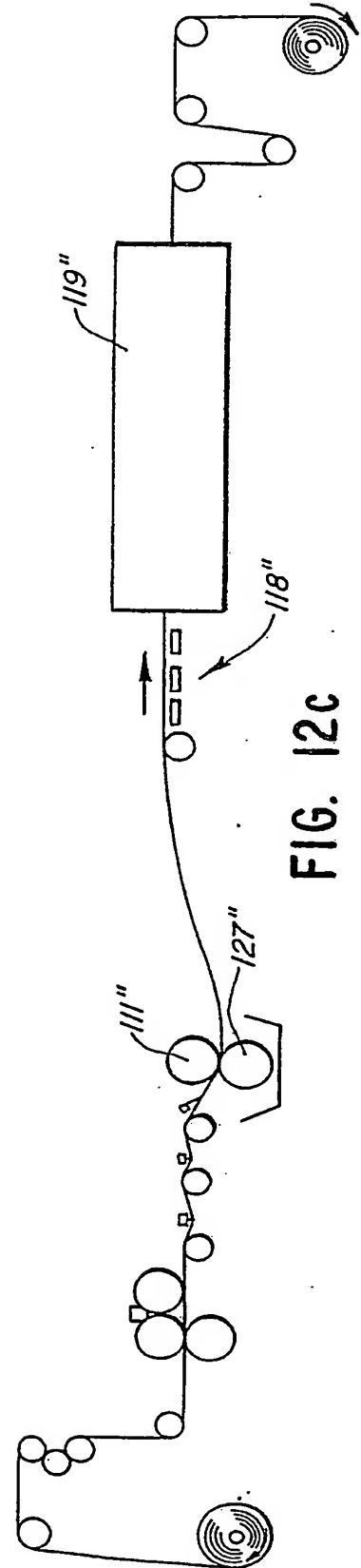
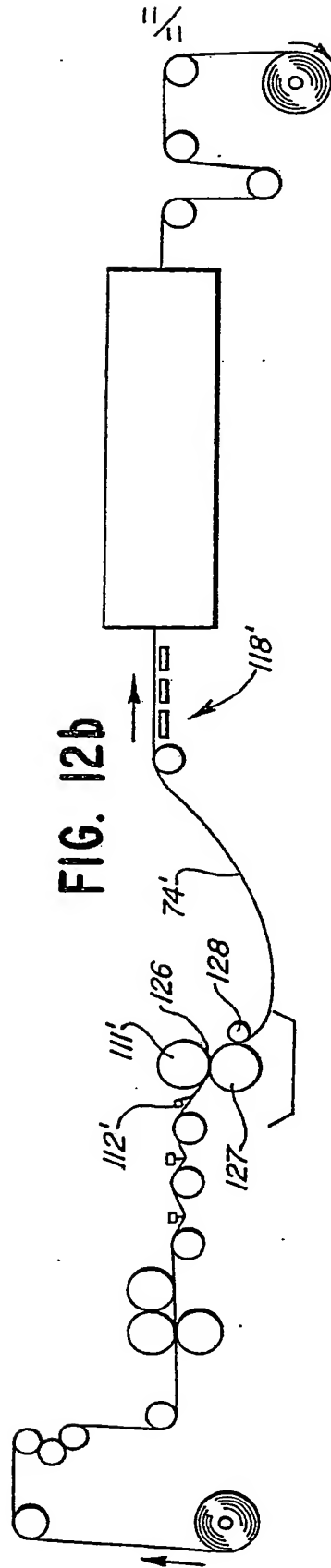
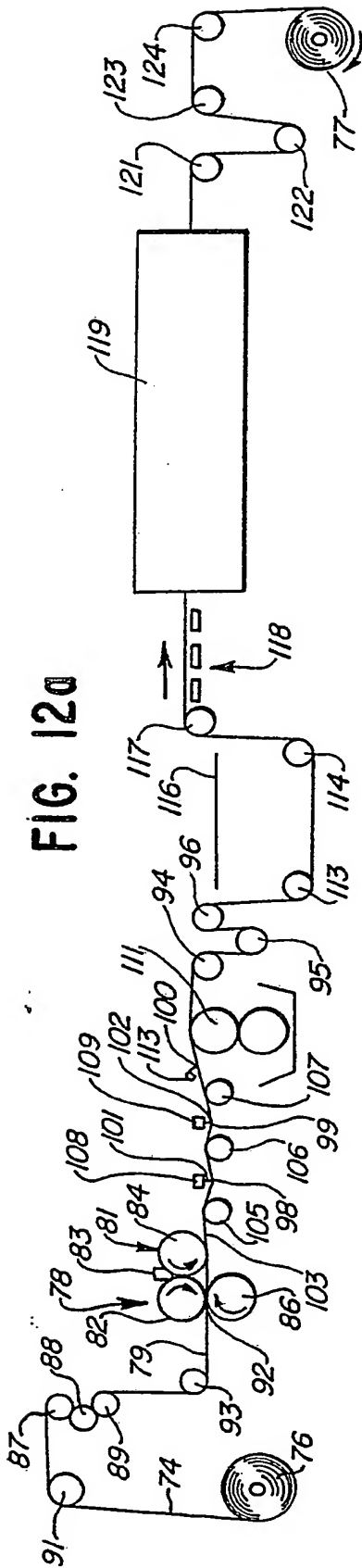


FIG. 11d PRIOR ART





INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US89/01009**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl 4 B32B 9/04; B05D 1/00

US Cl 427/393.4, 412; 428/266, 447

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
US	427/393.4, 412 428/266, 447

Documentation Searched other than Minimum Documentation
to the extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X Y	US, A, 4500584 (Modic), 19 February 1985. Entire Document	<u>1-10, 23-27,</u> <u>1-36</u>
X Y	US, A, 4051296 (Windecker), 27 September 1977. Entire Document	<u>1-10, 23-27</u> <u>1-36</u>
X Y	JP, A, 57-149559 (Unitika KK), 16 September 1982. Abstract	<u>1-36</u> <u>1-36</u>

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

23 MAY 1989

Date of Mailing of this International Search Report

23 JUN 1989

International Searching Authority

ISA/US

Signature of Authorized Officer

W. J. Van Balen
W. J. Van Balen